Theoretical description of nucleation in multicomponent system

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Abstract

The full theoretical analysis of the kinetics of multicomponent nucleation is presented. The relief of the free energy with surface excesses was analyzed, the valleys and ridges were described, their mutual interaction was studied. The new possibility to change the valley of nucleation is shown. The possibility to have one common valley instead of several neighbor ones which leads to the radical change in the height of the effective activation barrier and to the new value for the nucleation rate.

Introduction

Historically the problem of determination of the stationary rate of nucleation was primary investigated in one-dimensional approximation [1], [2]. The unique variable characterizing an embryo of a new phase was a number of molecules inside the embryo. Meanwhile, it is evident that the embryo has at least several characteristics, which have to be taken into account to give the adequate description of the nucleation process. That's why it is necessary to study the description of the nucleation process on the base of several characteristics of the embryo.

One can not pretend to take into account all characteristics of an embryo and to give the nucleation description on the base of all embryo characteristics. The kinetic aspects of the embryo formation are also far from clear interpretation. Even the mathematical structure of the theory of multi-dimension

nucleation is far from complete understanding. So, it is worth to start with the simple cases of multidimension description.

The simplest and the most evident example of multi-dimension description is a multicomponent nucleation. It means that the nucleation in mixture of vapors is studied. Here kinetic coefficients are determined extremely clear, the free energy of the embryo is also rather well known in general features.

The history of investigations of the binary nucleation is very rich. The number of publications concerning the binary nucleation is now greater than devoted to other domains of the nucleation theory. But already in the case of binary nucleation there appear many problems to solve. So, it is worth paying attention namely to multicomponent nucleation.

Until nowadays there is still no universal self consistent analytic approach which makes use of all previous theories or directly shows their errors. This task will be the goal of the present paper.

At first one has at least to mention approaches, which pretend to give original recipes for the stationary nucleation rate. Certainly, the classical expression for the free energy given by the standard thermodynamics has to be the starting point of a theory. In our analysis we ignore approaches suggesting some artificial correction terms or some reconsiderations without a solid thermodynamic base.

The microscopic corrections to the free energy given by classical thermo-dynamiocs [3], [4] are not the subject of our investigation, we consider only a task to describe nucleation at the relatively low supersaturations. Even this question is out of a true solution. We do not consider a normalising factor in an equilibrium distribution which evidently appear in the expression for the nucleation rate. This will be a subject of a separate investigation.

The first essential contribution to establish the binary nucleation rate was made by H.Reiss [5] who determined the rate of nucleation on the base of a steepest descent line in a near critical region. Solution of a kinetic equation presented by Reiss was corrected by Stauffer [6]. In the last paper the correct formula for the rate of nucleation in the square approximation of the free energy in the neighborhood of the critical embryo was given. Earlier the general ideas for the problem of overcoming the activation barrier in the multicomponent case were formulated by Langer [7] but one can not state that the publication [6] is a direct consequence of [7]. One has to stress that the constant direction of a flow in a neighborhood of the critical point was simply postulated in [6]. This constancy can be proven only with the help of the boundary conditions which was done in [8] where direct solution of the

kinetic equation was presented.

As it became clear after the solution of Trinkaus [9] the problem to determine the nucleation rate requires to decide whether the transition over the barrier really occurs at the critical point (the saddle point - here and later the critical point means the coordinates of the critical embryo). When there is a strong hierarchy between kinetic coefficients of absorption of different components one can see that flow of embryos can pass aside the critical region (the region near the critical point), but over the ridge far from critical point.

Solution of Stauffer implies the square approximation of the embryos free energy near the critical point. Solution of Trinkaus implies the linear approximation of the height of special activation barrier. But as it will be seen later there is no contradiction between approximations - both are suitable in corresponding situations.

Further analytical progress is associated with the appearance of many variations. Among them one can outline the refined Stauffer's solution presented by Berezhkovski and Zitserman [10] and conception of the genuine saddle point proposed by Li et al. [11]. One has to stress that these contributions did not radically change the already known formulas for nucleation rate but slightly corrected some known results. In this context it is also necessary to mention the publications of Shi and Seinfeld [12] and Wu [13].

Here we do not analyze the theories connected with the reconsidered free energy of the embryos formation taking their history from the famous publication of Lothe and Pound [14] and modifications of this approach to the case of multicomponent nucleation. Any new expression for the free energy will cause the new value of the nucleation rate but the mathematical structure of the derivation of the nucleation rate remains the same.

In the middle of 1990-ies the serious set of attempts to analyze the binary nucleation problems was presented in [15], [16].

In the last years one can outline the publications which analyze the same problems which have been already mentioned. The problem of boundary conditions was revised in publication of Wilemski and Fisenko [17]. The authors put the natural boundary conditions directly at the boundaries of a whole pre-critical region where these conditions are evident. But then it is necessary to solve the kinetic equation in the whole pre-critical and the near-critical region which was done in [17] only numerically.

The set of papers by Li, Nishioka, Maksimov [11] is devoted to give the definition of the generalized saddle point which can be used both in the

situation where the flow goes over the standard saddle point and in the situation of hierarchy where the solution of Trinkaus [9] takes place. This idea is certainly attractive but as it will be shown in this publication sometimes the nucleation occurs in a more complex way and can not be described in terms of the genuine saddle point even approximately. Moreover, the point of the Trinkaus' solution depends not only on the free energy but also on the derivatives along special directions.

The problem of transition of the binary case to the unary one was studied in [18] where the full analysis of this problem was given. Here we are not interested in this transition because the embryo with one molecule of a rare component can not be considered on the base of a standard thermodynamics in an approximation of a homogeneous liquid which is adopted in this publication.

Here we do not analyze numerous publications which combine the standard known approach with some artificial additions. Such combinations are rather typical for publications of Djikaev with coauthors (see, for example, [19]). In [19] the values of kinetic coefficients from the first passage time analysis are formally injected in the standard solution presented in [20] and the final formulas are presented. One has to mention that the first passage time analysis is based on some unknown characteristics (for example, the height of activation barrier for a molecule to penetrate inside the embryo) which can not lead to concrete results.

All mentioned publications in the binary nucleation do not make any profit from the topology of the relief of the free energy of the embryo. This task was solved in [20] where the structure of relief of the free energy in the capillary approximation was studied. It was shown that the relief of the free energy can be characterized as the straight channels, ridges and saddle points. In this publication the results of [20] will be widely used.

The formulation of the capillary approximation faces the difficulty known as the Renninger-Wilemski's paradox [21], [22]. Because of publications by Oxtoby and Kashiev [24] the thermodynamic background of the surface excesses is completely studied. To overcome this difficulty one has to write the Gibbs' absorption equation and to introduce surface excesses of components of the surface of tension. This leads to the difference of concentration in the surface layer and in the bulk of the embryo which was noted in [20]. But there further conclusions for kinetics of the process have not being made.

The structure of the free energy relief with surface excesses was investigated in [23] but only in thermodynamic aspects of the problem. The kinetic

4

features have not been considered in [23].

In [8] the kinetic equation was solved in the neighborhood of the critical embryo. The progress achieved in [8] was the appropriate formulation and account of boundary conditions. Certainly earlier the boundary conditions were mentioned in [9] but they were put in the infinitely far points where the structure of a free energy can not be seen in all details. Namely the necessity to conserve the boundary conditions at the low boundary of a near-critical region determines the conservation of the square form of the free energy in transformation presented in [8].

Having summarized the development of theoretical investigations in the binary nucleation one can state that despite the essential progress in this field there are still many problems to consider.

It is rather natural to construct the global picture of the nucleation including the case of the hierarchy between kinetic coefficients, surface excesses, etc. The unification of the free energy topological features with the already mentioned approaches is the main goal of this publication. This approach leads to many rather essential features of nucleation presented below. Moreover, some striking features changing the rate of nucleation in the order of magnitude will appear.

The structure of this paper is the following

- In the first part the main ideas of the capillary approximation are formulated and the free energy is constructed. Here the surface excesses are taken into account. The variables providing the simple form of the free energy are shown and their connection with the numbers of molecules in the embryo is established.

- The second part is devoted to the description of the near-critical region. It is shown that this region has the form similar to the case of the absence of the surface excesses. Here the hierarchy of evolution will be shown.

- The third part is devoted to the analysis of the Reiss' solution and the Stauffer's one. The plausible way to see the Reiss' formula will be shown. The moderate value of the difference between the Reiss' and the Stauffer's solution is justified. This is important for the possible ignorance of the slow or rapid variables of correcting order.

- The forth section analyzes the jump of the embryos from one channel

to another one. The situation of the near-equilibrium falling transition is considered here. The solution is found also in the discrete model.

- The fifth section considers the conception of the common valley. The equilibrium common valley transition is analyzed. It will be shown the new height of activation barrier. This value seriously differs from all known results.

- The sixth section analyzes the general picture picture of the nucleation rate formation. The case of the equilibrium saturation of the destination valley is studied.

- All results are summarized in the conclusion.

1 Thermodynamic basis

1.1 Capillary approximation

The main object involved in determination of the nucleation rate is the free energy of the isolated embryo. To give the description of the embryo one has to fix the variables of the state of the embryo. Assuming the thermal equilibrium of the embryo one can describe the embryo only by the numbers of molecules ν_i inside the embryo. These variables are extracted by following properties

- In elementary acts of evolution ν_i are changed separately. The step of change is one unit.

- Although the free energy even in capillary approximation is not diagonal the form of expression for the free energy is relatively simple.

In the capillary approximation the energy F ordinary taken in the thermal units is the sum of the bulk part B and the surface part Ω.

$$F = -B + \Omega$$

The ordinary expressions for B and Ω are following

$$B = \sum_i \nu_i \mu_i$$

$$\Omega = \gamma S$$

Here the sum is taken over all components of the embryo, μ_i are the differences of the chemical potentials counted from the equilibrium values (with a negative sign), S is the square of the surface of tension, γ is the renormalized surface tension.

The difference between the precise value of the free energy and the value in the capillary approximation referred as "correction terms" ($c.t.$) is supposed to be relatively small in comparison with $B + \Omega$. This situation takes place when the number of molecules

$$\nu_{tot} = \sum_i \nu_i$$

inside the embryo is very (strictly speaking infinitely) big

$$\nu_{tot} \gg 1 \tag{1}$$

The inverse number of molecules (i.e. ν_{tot}^{-1}) will be the small parameter of the theory. So,

$$F = -B + \Omega + c.t.$$

where $c.t.$ indicates correction terms with a property

$$|c.t.| \ll |F|$$

Ordinary the decomposition of correction terms on inverse radius r^{-1} of the embryo converges and F has the form

$$F = -B + \Omega + \sum_{k=-1}^{\infty} c_k r^{-k} + c_0 \ln r$$

Here c_k are the coefficients. One can also consider the last decomposition as an asymptotic decomposition. We shall accept the validity of this decomposition.

Ordinary this decomposition is taken with a finite number of terms

$$F = -B + \Omega + \sum_{k=-1}^{1 \div 2} c_k r^{-k} + c_0 \ln r \tag{2}$$

From the last decomposition it follows

$$|d\ c.t.| \ll |dF|$$

The last inequality is important in the justification of the linearization of the free energy.

While speaking about the capillary approximation one has to imply a whole set of assumptions beside the pure thermodynamic consideration. There are several ordinary used approximations included into the capillary approximation. These approximations are the following

- The surface tension is attributed to the dividing surface calculated on the base of the volume separation, i.e.

$$S = (\sum_i v_i \nu_i)^{2/3}$$

  where v_i are the volumes in a liquid phase. The formal factor $4\pi/(4\pi/3)^{2/3}$ is ordinary included into the effective surface tension.

- Values v_i, γ are taken from the case of a bulk liquid.

- To give expressions for μ_i one has to use some model. The most widely used model is the model of a liquid solution. The validity of this model requires

$$\nu_i \gg 1$$

  for every component. Certainly one can use other models and ignore these limitations. When $\nu_j = 1$ for some component, one can consider this component as a heterogeneous center. That's why the extension of the approximation of the regular solution up to $\nu_i = 1$ in [18] causes questions.

In this paper we shall use the model of solution.

To give a formula for chemical potential one can define a supersaturation as

$$\zeta_i = \frac{n_i}{n_{i\infty}}$$

where n_i is the molecular number density in the existing vapor and $n_{i\infty}$ is the molecular number density of the vapor saturated over the pure bulk liquid of component i with a flat surface. Then

$$\mu_i = \ln(\zeta_i) - \ln \xi_i - \ln f_i(\{\xi\})$$

Here it is supposed that the vapor is an ideal gas which gives the value for the first term in the r.h.s. as $\ln(\zeta_i)$. Ordinary it is assumed that the

concentrations ξ_i form a set $\{\xi\}$ of concentrations and the coefficients of activity f_i can depend on the whole set of activities.

For approximation of ideal solution all coefficients

$$f_i = 1$$

To know f_i one has to construct some model of solution or to use some experimental data.

- A special question concerns the definition of concentration. Ordinary the concentration is determined as

$$\xi_i = \frac{\nu_i}{\sum_j \nu_j} \tag{3}$$

  Sometimes this definition is also included into the ordinary auxiliary approximations of the capillary approach.

  This question is directly linked with the Wilemski-Renninger's paradox [21].

All assumptions made above are necessary for formula for the free energy in capillary approximation.

The presented formula for the free energy is rather transparent, but it faces the difficulty known as the Wilemski-Renninger's paradox. The difficulty is the following:

- It is known that in the critical embryo the Kelvin's relation

$$\frac{\mu_i}{v_i} = invariant$$

  has to be observed. This follows from the general thermodynamics and from the sense of chemical potentials.

  The last relation gives an equation for the concentration in the critical embryo.

- One can come to the same equation on concentration also by direct differentiation of expression for the free energy. For simplicity assume that v_i do not depend on concentration. This gives

$$\frac{\partial F}{\partial \xi_i} = 0$$

9

i.e.
$$0 = -\mu_i - \sum_j \frac{\partial \mu_j}{\partial \nu_i} \nu_j + \frac{2}{3} \gamma (\sum_j v_j \nu_j)^{-1/3} v_i + S \frac{\partial \gamma}{\partial \nu_i}$$

Here it is supposed that v_i do not depend on concentration.

One has to recall that the coefficients of activity f_i satisfy the Gibbs-Duhem's equations

$$\sum_i \xi_i d\mu_i = 0$$

which put a restriction on the coefficients of activity.

$$\sum_i \xi_i d \ln f_i = 0$$

Moreover the Gibbs-Duhem equation can be written as

$$\sum_j \frac{\partial \mu_j}{\partial \nu_i} \nu_j = 0$$

Then the differentiation becomes very simple and leads to

$$\frac{\partial F}{\partial \xi_i} = 0 = -\mu_i + \frac{2}{3} \gamma (\sum_j v_j \nu_j)^{-1/3} v_i + S \frac{\partial \gamma}{\partial \nu_i}$$

Then one can come to the widely known Kelvin's equation only if the derivative $\partial \gamma / \partial \xi_i$ is zero. So, the formal recipe is to forbid the differentiation of the surface tension on concentration. Since the last equation comes from the foundations of thermodynamics it means that something is irrelevant in the previous formula for the free energy.

In the case when v_j depend on concentration we have

$$\frac{\partial F}{\partial \xi_i} = 0 = -\mu_i - \sum_j \frac{\partial \mu_j}{\partial \nu_i} \nu_j + \frac{2}{3} \gamma (\sum_j v_j \nu_j)^{-1/3} [v_i + \sum_j \frac{\partial v_j}{\partial \nu_i} \nu_j] + S \frac{\partial \gamma}{\partial \nu_i}$$

But the Gibbs-Duhem equation has to be here the following one

$$-\sum_j \frac{\partial \mu_j}{\partial \nu_i} \nu_j + \frac{2}{3} \gamma (\sum_j v_j \nu_j)^{-1/3} \sum_j \frac{\partial v_j}{\partial \nu_i} \nu_j = 0$$

which leads to the same conclusions.

10

As the result there appeared a formal recipe not to differentiate the surface tension. At first it was the artificial recipe but later the justification of this recipe was given on the base of the Gibbs dividing surfaces formalism.

To resolve this difficulty one has to add to the free energy some new contributions connected with the surface excesses. It will be done later.

Now we return to consideration of the properties of F.

The leading idea here is the extraction of the mentioned small parameters ν_i^{-1}. Recall that conditions are rather far from the second order phase transition. If we accept that the surface layer has a finite thickness d, then in the limit $r \to \infty$ (where r is the radius of the embryo) one can see that correction terms ($c.t.$) are really relatively small in the following sense

$$|B| \gg |c.t.| \qquad |\Omega| \gg |c.t.|$$

$$|\frac{\partial c.t.}{\partial \nu_i}| \ll |\frac{\partial B}{\partial \nu_i}| \qquad |\frac{\partial c.t.}{\partial \nu_i}| \ll |\frac{\partial \Omega}{\partial \nu_i}|$$

$$|\frac{\partial^2 c.t.}{\partial \nu_i^2}| \ll |\frac{\partial^2 \Omega}{\partial \nu_i^2}|$$

These inequalities are valid for absolute values.

These inequalities is a new result and they will be widely used below. Their validity can be proven analytically.

1.2 The form of the free energy

To see the structure of the free energy one can introduce the extensive variable

$$V = \sum_i v_i \nu_i$$

Certainly V is a volume of the embryo. Then

$$F = \gamma V^{2/3} - b(\xi) V$$

with the generalized chemical potential

$$b = \frac{\sum_j \mu_j \xi_j}{\sum_j v_j \xi_j}$$

The generalized chemical potential allows an interpretation

$$b = \frac{<\mu>}{<v>}$$

as the ratio of the mean chemical potential excess and the mean volume per one molecule in the embryo.

One can take also as an extensive variable the total number of molecules inside the embryo

$$\nu_{tot} = \sum_i \nu_i$$

Then the free energy can be written in a following way

$$F = \gamma(\sum_i v_i \xi_i)^{2/3} \nu_{tot}^{2/3} - \nu_{tot} \hat{b}(\xi)$$

where

$$\hat{b}(\xi) = \sum_i \mu_i \xi_i$$

and the renormalized surface tension

$$\hat{\gamma} = \gamma(\sum_i v_i \xi_i)^{2/3}$$

appears.

One has also to mention the possibility to take as external variable the surface energy in the power $3/2$, i.e.

$$\varsigma = \gamma^{3/2} \sum_i v_i \nu_i$$

used in [20]. Then the free energy has the form

$$F = -b_p(\xi)\varsigma + \varsigma^{2/3}$$

where the generalized chemical potential is

$$b_p = \frac{\sum_j \mu_j \xi_j}{\sum_i \gamma^{3/2} v_i \xi_i} = \frac{b}{\gamma^{3/2}}$$

The third possibility used in [20] is the most preferable because here the free energy has the most simple form and in the "surface" term the factor depending on concentration is absent.

The question to discuss is what we shall take as an extensive variable - the variable proportional to the volume or the value proportional to the number of molecules? Thermodynamics does not give an answer because asymptotically these values are proportional.

But the problem to take into account the Renninger-Wilemski's paradox remains here our of attention. To overcome this difficulty one has to include into description the surface excesses of components. To take these excesses one has to choose the surface accurately. The most preferable choice is to choose as the surface the surface of tension because the surface tension can be attributed to this surface without corrections. At this surface all components have the surface excesses ψ_i but the surface tension can be attributed namely to this surface. In the first (rough) approximation these values are proportional to the square S of the surface of tension

$$\psi_i = \varrho_i S$$

Parameters ϱ_i are supposed to be independent on S and have to be given by the theory of a liquid state.

The square of the surface of tension can be approximately calculated as

$$S = (\sum_i v_i(\nu_i - \psi_i))^{2/3}$$

Certainly, there exists a difference between a surface of tension and the surface covering the volume of the embryo. But since the sense has only $S\gamma$ one can attribute this difference to the value of γ.

Here we omit the constant factor having included it into the surface tension γ. Hence,

$$\psi_i = \varrho_i(\sum_i v_i(\nu_i - \psi_i))^{2/3}$$

The last relation is not a formula for ψ_i but an equation. It can be solved by iterations. These iterations are based on a small parameter ψ_i/ν_i. The smallness of these parameters at $\nu_i \to \infty$ is evident. The first approximation

$$\psi_i = \varrho_i(\sum_i v_i\nu_i)^{2/3}$$

is already suitable as a leading term under the conditions (1). The second iteration

$$\psi_i = \varrho_i(\sum_i v_i(\nu_i - \varrho_i(\sum_j v_j\nu_j)^{2/3}))^{2/3}$$

will refine the solution. The complexity of dependence of ψ_i on ν_i is the certain difficulty.

The value of concentration ξ_i has now to be redefined as

$$\xi_i = \frac{\nu_i - \varrho_i S}{\sum_j (\nu_j - \varrho_j S)}$$

As an extensive variable it is natural to choose the straight analog of ς, namely

$$\varsigma = (S\gamma)^{3/2} = \sum_i v_i (\nu_i - \psi_i)\gamma^{3/2}$$

But this choice does not lead to the "true" form of the free but to

$$F = -\sum_j \lambda_j \mu_j - \sum_j \varrho_j \mu_j \frac{\varsigma^{2/3}}{\gamma(\xi)} + \varsigma^{2/3}$$

with

$$\lambda_i = \nu_i - \psi_i$$

Here the dependence γ on $\{\xi\}$ is the source of difficulties. Certainly,

$$\frac{\lambda_i}{\lambda_j} = \frac{\xi_i}{\xi_j}$$

One can introduce another set of variables. Now instead of ς one has to choose the extensive variable

$$\kappa = S^{3/2}(\gamma - \sum_i \varrho_i \mu_i)^{3/2}$$

In these variables the free energy F has the form

$$F = -\kappa b_g(\xi) + \kappa^{2/3} \tag{4}$$

with the generalized chemical potential

$$b_g = \frac{\sum_i \lambda_i \mu_i}{\kappa}$$

or

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{\kappa}$$

14

One has to show that b_g does not depend on κ. To fulfill this derivation one can come to

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{S^{3/2}(\gamma - \sum_k \varrho_k \mu_k)^{3/2}}$$

or

$$b_g = \sum_i \xi_i \mu_i \frac{\sum_j \lambda_j}{(\gamma - \sum_k \varrho_k \mu_k)^{3/2} \sum_l v_l \lambda_l}$$

It can be also presented as

$$b_g = \sum_i \xi_i \mu_i \frac{1}{(\gamma - \sum_k \varrho_k \mu_k)^{3/2} \sum_l v_l \xi_l} \tag{5}$$

The last relation evidently shows that b_g is really a function of ξ. The dependence on κ is absent.

One can use expression (5) to clarify the Renninger-Wilemski's paradox. According to the Gibbs' absorption relation

$$d\gamma = d \sum_j \varrho_i \mu_i$$

the derivative of the surface tension on concentration is cancelled by the corresponding derivatives of ϱ_i on ξ. So, if we write b_g without surface excesses as

$$b_g = \sum_i \xi_i \frac{1}{\gamma^{3/2} \sum_j v_j \xi_j}$$

we have to forbid the differentiation of γ on concentration. Now the Renninger-Wilemski's paradox is explained. It is necessary to stress that the reason is not the formal Gibbs' absorption equation, but the difference of concentrations in the bulk solution from the integral values.

Although the the new variables ensure the simple form of the free energy their connection with "initial" variables ν_i is rather complex. One has to see how on the base κ, ξ_i it is possible to reconstruct ν_i. The procedure is the following:

- On the base of ξ_i we know μ_i, then we get $\gamma - \sum_i \varrho_i \mu_i$.

- This gives a value of

$$S = \kappa^{2/3}/(\gamma - \sum_i \varrho_i \mu_i)$$

- On the base of S having presented S as

$$S = \sum_i v_i \lambda_i = \sum_i v_i \xi_i \sum_j \lambda_j$$

we get $\sum_i \lambda_i$.

- Since $\lambda_i = \xi_i \sum_j \lambda_j$ we get all λ_i.

- Then

$$\nu_i = \lambda_i + \varrho_i(\xi) S$$

and we know all ν_i.

The inverse transformation can not be made by explicit formulas, the problem to find[1] ϱ on the base of ν has been considered above. When ϱ is found then λ is known. This gives ξ and κ.

The main new facts found here are the following:

- The variables giving the simple expression for the free energy with surface excesses are found.

- The recipe to get the initial variables on the base of the new ones is given

1.3   The structure of the free energy relief

The functional form (4) has some consequences analogous to those considered in[2] [20]. But now this form takes into account the surface excesses of an embryo. Here the form (4) ensures the following properties of the free energy of an embryo

- One can see the channels of nucleation defined by equations

$$\frac{\partial b_g}{\partial \xi_i} = 0$$

$$\frac{\partial^2 b_g}{\partial \xi_i^2} < 0$$

Along these channels the equilibrium density of distribution has a maximum (but the real distribution coincides with the equilibrium one only in the part of the pre-critical region)

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[1]When the index is absent it means that the whole set is considered.
[2]In [20] the free energy without surface excesses was considered.

- Because of the Gibbs-Duhem's equation the variables ξ_i in differentiating of b_g are separated. This leads to the approximately zero value of the cross derivatives $\partial^2 b_g / \partial \xi_i \partial \xi_j$.

- One can see the separation lines of nucleation defined by equations

$$\frac{\partial b_g}{\partial \xi_i} = 0$$

$$\frac{\partial^2 b_g}{\partial \xi_i^2} > 0$$

  Along the separation lines the equilibrium density of distribution has a minimum.

- In one channel there is only one saddle point. Certainly, this takes place only in the capillary approximation. This saddle point has a coordinate κ_c determined from the following equation

$$\kappa_c = \left(\frac{2}{3 b_g(\xi_c)}\right)^3$$

  Here ξ_c is the coordinate of the channel.

- The amplitude value of the free energy F_c in the channel is given by the formula

$$F_c = \frac{1}{3} \kappa_c^{2/3}$$

  Here one can see the Gibbs' equation and now it is clear that namely $\kappa^{2/3}$ is the true surface energy, but not γS as it seems from the first point of view. One has to attribute to the surface energy all energy like contributions with the space dimension 2 (or 2/3 in relative units).

- All channels are independent - the embryos starting from the origin of coordinates will use only one separate channel to go to the supercritical region where they begin to grow irreversibly. The nucleation flow will mainly go through the channel with minimal κ_c or maximal b_g. This remark concerns the case where there is no strong hierarchy between kinetic coefficients of absorption.

One can see that the picture of nucleation is rather simple, but this simplicity was observed for the free energy with the surface excesses for the first time here. This is the new result of this section.

17

1.4 The form of the near-critical region

As it has been mentioned at the beginning the set of natural variables is ν_i. The elementary kinetic act of absorption leads to the change

$$\nu_i \to \nu_i \pm 1$$

So, it is necessary to establish connection between κ, ξ and ν at least approximately.

Denote by the subscript o the values when all surface excesses are zero. Then the theory is very simple and one can get the connection between κ_o, ξ_o and ν_o in a very transparent manner. From ν_0 to κ_0, ξ_0 one can get by

$$\kappa_0^{2/3} = \gamma \sum_i v_i \nu_{i0}$$

$$\xi_{i0} = \nu_{i0} / \sum_j \nu_{j0}$$

Inverse transformation is given by the chain formulated above. So, it is quite easy to write the kinetic equation for the case of the absence of excesses.

The above consideration shows the role of the case with zero excesses. Hence, this case will be the base to construct the description in the general case.

Return now to the general case.

One can define the near-critical region as the region where

$$|F - F_c| \leq 1$$

This is quite analogous to the one component case. But here we consider the near-critical region associated with the given channel. Then it is necessary that this region has to be closer to this point than the separation lines.

One can define the positive size $\Delta\kappa$ of the near-critical region along the channel of nucleation as

$$F(\kappa_c \pm \Delta\kappa, \xi_c) = F_c - 1$$

Here ξ_c is the coordinate of some channel. Certainly, we get two values $\Delta_1\kappa$ and $\Delta_2\kappa$ corresponding to the positive and to the negative shift. In the square approximation of the free energy

$$\Delta_1\kappa = \Delta_2\kappa = 3\kappa^{2/3} \tag{6}$$

When $\nu_i \gg 1$ for all i the square approximation is rather accurate.

Analogously one can define the characteristic sizes $\Delta\xi_i$ according to relation

$$F(\kappa_c, \xi_c \pm \Delta\xi_i) = F_c + 1$$

Certainly, we get two values $\Delta_1\xi_i$ and $\Delta_2\xi_i$ corresponding to the positive and to the negative shift. In the square approximation

$$\Delta_1\xi_i = \Delta_2\xi_i = |\frac{\partial^2 b_g}{2\partial\xi_i^2}|^{-1/2}\kappa^{-1/2} \tag{7}$$

When $\nu_i \gg 1$ for all i and there is no singular behavior of generalized chemical potential then the square approximation is valid.

Certainly, it is necessary that the channels have to be separated, i.e. the height of the separation line has to be several thermal units higher than the height of the channels. This has to take place at κ near the critical value.

We define the reduced near-critical region as the region where $|\kappa - \kappa_c| \leq \Delta\kappa$, $|\xi_i - \xi_{ic}| \leq \Delta\xi_i$. This definition differs from the ordinary definition of the near critical region as extracted by condition $|F - F_c| \leq 1$.

In the multi-dimensional case there exists long tails near lines $F = F_c$. To illustrate it one can use the square approximation, then the curves $F = F_c + 1$ and $F = F_c - 1$ are hyperbolic ones with common asymptotics which are straight lines.

We shall define the tails as the regions corresponding to $|F - F_c| \leq 1$ and $|\xi_i - \xi_{ic}| > \Delta\xi_i$, $|\kappa - \kappa_c| > \Delta\kappa$.

Actually, the following statements can be proven analytically:

- One can show that the tails do not play any essential role in formation on the total nucleation flow.

- Then it is possible to reduce the near-critical region up to the following domain

$$|\xi_i - \xi_{ic}| \leq \Delta\xi_i$$
$$|\kappa - \kappa_c| \leq \Delta\kappa$$

Here and later we shall imagine the reduced near-critical region speaking about the near-critical region.

Now one can see that the relative sizes of the near-critical region are small

$$|\xi_i - \xi_{ic}| \ll \xi_i$$

19

$$|\kappa - \kappa_c| \ll \kappa$$

Ordinary this smallness is implied when the kinetic coefficient of absorption is supposed to be a constant value. Here this smallness will help to prove the following main result of this section:

- **In the near-critical region the function $F - F_c$ as a function of variables $\kappa - \kappa_c$, $\xi_i - \xi_{ic}$ for every i has practically the same behavior as the function $F_o - F_{co}$ as a function of variables $\kappa_o - \kappa_{co}$, $\xi_{io} - \xi_{ico}$. At least the relative difference is small:**

$$\frac{|(F(\nu_i - \nu_{ic}) - F_c) - (F_o(\nu_{io} - \nu_{ico}) - F_{co})|}{(F_o(\nu_{io} - \nu_{ico}) - F_{co})} \ll 1$$

  The explanation and the idea of the proof is rather simple. Really, the correction terms to which the excesses belong begin to be essential only when the surface term cancels the bulk term. But as it clear from the sequential differentiation this can take place only in the first derivative. Starting from the second derivative the contribution from the bulk term is zero and this compensation can not take place. This effect is taken into account by the shift of ν_{ic} instead of ν_{ic0}. So, here the influence of correction termms is negligible.

The last result allows to write the kinetic equation in ν_i variables taking into account the surface excesses by a simple shift. This takes place only in the near-critical region. This result is new.

1.5 The place of the Renninger-Wilemski's effect

The "paradox" of Wilemski and Renninger occupies so important place in the multicomponent nucleation that from the first point of view it seems that this is the real effect taking place in the leading term of capillary approximation. Below it is shown that this effect has an order of correction. To see this effect one can redefine κ as $S^{3/2}$ and forget about excesses.

Really, from equation

$$\frac{\partial F}{\partial \xi}\Big|_{\kappa=fixed} = \frac{\partial \gamma}{\partial \xi}\kappa^{2/3} + \frac{\partial b_g}{\partial \xi}\kappa\gamma^{3/2}$$

it is seen that the first term $\frac{\partial \gamma}{\partial \xi} \kappa^{2/3}$ with the derivative $\frac{\partial \gamma}{\partial \xi}$ has a correction order $\kappa^{2/3}$

$$\frac{\partial \gamma}{\partial \xi} \kappa^{2/3} \sim \kappa^{2/3}$$

in comparison with the second term $\frac{\partial b_g}{\xi} \kappa \gamma^{3/2}$ having the order κ

$$\frac{\partial b_g}{\xi} \kappa \gamma^{3/2} \sim \kappa$$

We extract this result which is explicitly outlined for the first time here because of its importance for the reconstruction of the logical self-consistency of thermodynamics. Only the correcting order of the term with the derivative of the surface tension allows to ignore it in the main order and to return the leading role of the ordinary capillary approximation.

Since the formal recipe to resolve the Renninger-Wilemski's paradox is to forbid the differentiation of γ on concentration then the equation on concentration will be different. It would cause the impression that there is a shift in a leading term. The correct answer is that this result causes the shift in F_c which has a correction order as it follows from the last equation.

The necessity to develop the theory with surface excesses is evident because the surface excesses will essentially shift the position of the near-critical region. The shift is many times greater than the size of the near-critical region. The shift has the order κ (because there is another equation on concentration - the derivative of γ on ξ is cancelled) while the size of the near-critical region has the order $\kappa^{1/2}$.

One can treat the surface tension as a coefficient in the first correction term proportional to the surface of the embryo. The coefficients at $\kappa^{1/3}, \ln \kappa, \kappa^{-1/3}$, etc. depend on intensive variables (concentrations is one example). Their derivatives will be cancelled by derivatives of corresponding excesses. The structure will resemble the Renninger-Wilemski's paradox. But here the dimension of "surface" will be $\kappa^{1/3}, \ln \kappa, \kappa^{-1/3}$, etc. This effect will be called as "generalized cancellation of derivatives on intensive variables".

One to note that the same procedure can be effectively applied for all other correction terms. Rigorously speaking to determine the form of the near-critical region one has to take the expression for F with correction terms up to the order which causes the shift of position of the near-critical region. Now it is clear that the effect of all correction terms will be quite similar to

the already described one.

2 Channels and separation lines

2.1 Similarity of the near-critical relief

Although the Renninger-Wilemski's effect has a correction order it is worth taking it into account. The main reason is the following:

- The relative sizes of the near-critical region is very small. Really, from (6) it follows that
$$\frac{\Delta \kappa}{\kappa_c} \sim \kappa_c^{-1/3} \ll 1$$
and the relative size in κ-scale is small. From (7) it follows that
$$\Delta \xi_i / \xi_i \sim \kappa^{-1/2}$$
and the relative size in the ξ_i scale is small also. Then it is clear that the relative size in ν_i scale will be
$$\nu_i / \nu_{ic} \sim \nu_i^{-1/3}$$
Namely these estimates allow to put in the near-critical region the kinetic coefficient W_i^+ of absorption of the molecule of i-th component to the constant value W_{ic}^+ corresponding to the critical embryo
$$W_i^+ \approx W_{ic}^+$$

So, the relatively small error in the determination of the coordinates ν_i can remove embryo out of the near-critical region which makes the consideration of kinetic equation without surface excesses in the near-critical region useless.

Beside this one has to take into account that the elementary transitions are written in the ν-scale
$$\nu_i \to \nu_i \pm 1$$
and the free energy is written explicitly (with the surface excesses account) in variables κ, ξ_i. So, it is necessary to have the a very precise transformation between ν_i and κ, ξ_i. This forms the problem.

Although the transformation from κ, ξ_i to ν_i exists it is very complex. The inverse transformation has not been found explicitly. So, it is necessary to establish the approximate connection. The following statement establishes this connection

- The function $F - F_c$ as a function of $\nu_i - \nu_{ic}$ approximately coincides in the near-critical region with the behavior of $F_0 - F_{0c}$ as a function of $\nu_i - \nu_{ic0}$:

$$F_0(\nu_{ic0} + y_i) - F_{c0} \approx F(\nu_{ic} + y_i) - F_c$$

This property can be called as the approximate similarity of the free energy relief.

Here this fact is established for $\{\nu_i\}$ variables while earlier the same conclusion was made for $\kappa, \{\xi\}$ variables.

The idea of the proof of this property is based on the simple remark that the terms produced by the surface excesses can be important only when the terms produced by the bulk and surface contributions are cancelled. In the near-critical region this occurs only in the first derivative over ν_i at the critical embryo. Cancellation in high derivatives is impossible[3]. Here we use the form $F = \sum_i \mu_i \nu_i - \gamma S$ and differentiate it over ν_i. This ensures the similarity of relief.

Now one can propose the following sequence of actions

- at first one has to solve equations for the characteristics of the critical embryo

- then one has to solve the kinetic equation without excesses but in shifted coordinates.

Certainly, the similarity of relief takes place both in ν_I coordinates and in κ, ξ_i coordinates.

Analogously one can one can prove the small relative role of microscopic corrections in the value of $dF_c/d\zeta_i$ which is used in construction of the global evolution of the phase transition. Here the formula (2) has to be used and it has to be taken into account that the coefficients in this formula are constant.

2.2 The form of pre-critical region

One can see the following important property:

- **The critical embryo can not have $\xi_i = 0$**

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[3]Since the high derivatives of the bulk contribution are zero.

It can be seen from the explicit form of μ_i

$$\mu_i = \ln \zeta_i + \ln \xi_i + \ln f_i(\xi)$$

Recall that here ζ_i is the supersaturation of i-th component defined as

$$\zeta_i = \frac{n_i}{n_{ii}}$$

n_i is the molecular number density of vapor of i-th component, n_{ii} is the molecular number of the pure saturated vapor of i-th component. The second term is caused by the standard entropy of mixing, the third term characterizes the deviation of mixture from the ideal solution, here f_i is the phenomenological coefficient of activity.

Then one can see that at $\xi_i \to 1$ the situation of dilute solution takes place. Then the Henry's law states that the situation is close to the ideal solution, then $f_i = 1$ and there are no correction terms. Then one can see that

$$\frac{db_g}{d\xi_i}\big|_{\xi_i=1} = \infty$$

and the condensation into the pure component is forbidden. Analogously

$$\frac{db_g}{d\xi_i}\big|_{\xi_i=0} = -\infty$$

Earlier the analogous estimates were formulated in [20] for ξ_{i0}. Then from (6) and (7) it follows that the widths $\Delta \nu_i$ along ν_i satisfy

$$\Delta \nu_i \gg 1$$

for all i. These estimates ensure the possibility of continuous description of evolution in the kinetic equation.

In the absence of the strong hierarchy between coefficients of absorption one can define the pre-critical region by two conditions

- by inequality
$$F < F_{cm} - 1$$
  where F_{cm} is the minimal activation barrier among different channels.

- by requirement that this region has to be continuous and the origin belongs to this region.

One can prove that in this region the quasi stationary equilibrium state takes place. Here the absence of the hierarchy of kinetic coefficients plays the principal role.

Now one can investigate the form of the pre-critical region in ν_i variables. It looks like a star and the needles are going along the bottoms of channels. Certainly due to restrictions $\nu_i \geq 0$ there is only one quarter of a star. In $\kappa, \{\xi\}$ variables it looks like a brush.

If in every channel we put the value F_c corresponding to this channel, the shortest needle is the main one. The shortest needle (in κ, ξ plane) corresponds to the lowest barrier and, hence, it is the main needle through which the nucleation takes place.

If the level F_c is chosen as F_{cm} and it is one and the same for all channels then the main needle is the longest one

To see the relaxation to the equilibrium distribution we need to determine the minimal diameter of this star. It is given by the following relation

$$-\kappa_{min} b_{g\ min} + \kappa_{min}^{2/3} = F_{cm} - 1$$

Here $b_{g\ min}$ is the minimal value of b_g. So, if $|b_{g\ min}|$ does not go to infinity, one can easily see the finite value of κ_{min} and the connection of channels.

The last consideration solves the problem of connection of channels of nucleation. The problem was that the behaviour of channels near the origin where the surface excesses can play the leading role was unclear. So, one could not say whether the channels are connected or no. Now the concrete position of channels near origin is not important.

The only condition is the restriction on $b(\xi)$ - this function can not go to $-\infty$ at some concentrations.

2.3 Characteristic sizes of near-critical region.

Consider the variables parallel to ξ_i, κ and having the scale of ν_i. These variables are

$$\nu_{par} \simeq \frac{\kappa n}{\gamma^{3/2} \sum_i^n v_i}$$

$$\nu_{i\ perp} \simeq \nu_{par} \xi_i$$

Here it is supposed that all v_i have the same order of values. The total number of components n is not supposed to be a big parameter.

Then the halfwidths along ν_{par} and $\nu_{i\ perp}$ satisfy the following estimates

$$\Delta \nu_{par} \sim \kappa^{1/6} \Delta \nu_{i\ perp}$$

$$\Delta \nu_{par} \sim \kappa^{2/3} \sim \nu_{tot}^{2/3}$$

$$\Delta \nu_{perp} \sim \kappa^{1/2} \sim \nu_{tot}^{1/2}$$

The time of establishing of the stationary state along $\nu_{par}, \nu_{i\ perp}$ is given by

$$t_{r\ par} sim (\frac{W^+}{\Delta^2 \nu_{par}})^{-1}$$

$$t_{r\ iperp} \sim (\frac{W^+}{\Delta^2 \nu_{i\ perp}})^{-1}$$

Here all kinetic coefficients of absorption are supposed to have one and the same order of value which is marked by W^+.

Then we come to the following strong inequality

$$\frac{t_{r\ par}}{t_{r\ iperp}} \sim \kappa^{1/3} \gg 1$$

This equation states the hierarchy in the near critical region. Earlier this hierarchy was established in [25] for the situation without surface excesses. Here it is done for the presence of the surface excesses.

To see this property the main effort was spent to show the similarity of forms of the free energy relief. Then one can come to the hierarchy rather automatically.

The mean characteristic time t_u to overcome the near-critical region for the embryo at the bottom the channel at the boundary of the near-critical and pre-critical regions has the order of $t_{r\ par}$

$$t_u \sim t_{r\ par}$$

Then we come to the following strong inequality

$$\frac{t_u}{t_{r\ iperp}} \sim \kappa^{1/3} \gg 1$$

It means that along $\nu_{i\ perp}$ there is a quasi equilibrium.

26

2.4 Advantages of hierarchy

On the base of hierarchical inequalities one can see that along $\nu_{i\ perp}$ or ξ_i there is quasi equilibrium. Then the distribution function $n(\{\nu_i\})$ which can be transformed into $n(\nu_{par}, \{\nu_{i\ par}\})$ can be presented as

$$n(\nu_{par}, \{\nu_{i\ par}\}) = N_{par}(\nu_{par})n_{eq}(\{\nu_{i\ perp}\})$$

where N_{par} plays the role of the amplitude of the known equilibrium distribution and n_{eq} is given by

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(-F(\nu_{par}, \{\nu_{i\ perp}\}))$$

or more convenient

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(F(\nu_{par}, \{\nu_{i\ perp}\}) - F(\nu_{par}, \{\nu_{i\ perp\ b}\}))$$

where b marks the coordinate of the bottom of the channel.

Then there remains only the task to determine the amplitude N_{par}. This is a simple one-dimensional problem of nucleation. One can easily solve it.

Reduction the problem of nucleation to the one dimensional case allows to solve more complex situations. At first one can see that when the characteristic width of equilibrium distribution seriously changes it leads to the change of the effective free energy in N_{par}. Really the effective free energy looks like

$$F_{eff} = F - \ln \Delta_{eq}\nu$$

where

$$\Delta_{eq}\nu = \left(\sum_{\nu_{perp}} n_{eq}(\nu_{perp}) \right)^{-1}$$

In the majority of cases the summation in the last formula can be replaced by integration

$$\Delta_{eq}\nu = \left(\int_{-\infty}^{\infty} n_{eq}(\nu_{perp})d\nu_{perp} \right)^{-1}$$

Here the region of integration is formally put to an infinite one, actually one has to integrate over the region near the bottom of the channel where n_{eq} is essential.

The further simplification is the following: one can take the last integral in square approximation for the equilibrium distribution:

$$n_{eq}(\{\nu_{i\ perp}\}) \sim \exp(-F_b)\prod_j \exp\left(-\frac{\partial^2 F(\nu_{par}, \{\nu_{i\ perp}\})}{2\partial\nu_{j\ perp}^2}\Big|_{\nu_{i\ perp}=\nu_{i\ perp\ b}}(\nu_{j\ perp}-\nu_{j\ perp\ b})^2\right)$$

This allows to take integrals explicitly.

Then the effective free energy is given by

$$F_{eff} = F - \sum_j \ln \frac{\pi^{1/2}}{\sqrt{\frac{\partial^2 F(\nu_{par}, \{\nu_{i\ perp}\})}{2\partial \nu_{j\ perp}^2}}\big|_{\nu_{i\ perp} = \nu_{i\ perp\ b}}}$$

Later one has to solve one-dimensional nucleation problem with the effective free energy instead of the initial free energy. As it will be shown later by demonstration of the plausible derivation of Reiss' formula one has to be very attentive at this step.

Ordinary in the near-critical region the value $\Delta_{eq}\nu$ is constant and there is no peculiarities in behavior of F_{eff}. Certainly, in the square approximation the is an explicit solution of Stauffer. But the approach based on hierarchy leads to final analytical results in more complex and may be exclusive cases. Really, here the square approximation was taken only as an illustration.

One has to clarify the place of the presented approach in the task to determine the nucleation flow. Ordinary to justify the total square approximation in the near critical zone and to use the Langer-Stauffer's approach one has to adopt some approximations including the smooth behavior of the derivative of b_g near the bottom of the channel. But there is no clear evidence of the regular behavior of b_g near the bottom. So, the approach based on the hierarchy is preferable.

On the base of hierarchy one can also see many interesting and important facts:

- At first we see that the quasi-unary condensation can not be described in terms of the square approach. A direct transformation of the formulas appeared in the Langer-Stauffer's approach does not lead to the formulas of the unary nucleation. This occurs because inevitably the square approximation has to be violated. So, we come to **the impossibility of description of the quasi-unary nucleation in terms of the standard Stauffer's binary nucleation approach.**

- The next consequence of general results is the impossibility of situation of the inverse direction proposed by Zisterman-Berezhkovskii, where [10] the Stauffer's approach meets difficulties. Really, now it is clear that valleys have to be directed to the origin, but not at the perpendicular direction as it is supposed in the consideration of Zisterman and Berezhkovskii.

One has to mention that the thermodynamics is rather formal and can give essential corrections to the initial variant of the theory if some other expressions for chemical potentials and surface energy are taken. Certainly, these expressions have to be the matter of discussion. But one can not deny the possibility to come to the situation where the square approximation is not suitable and one has to follow the approach suggested here.

Here we suppose that these expressions are already given. They are some external information for the theory developed here.

3   Stauffer's and Reiss' solutions

The main goal in the investigation of the multicomponent nucleation is to get essential corrections in comparison with the already known approaches. For this purpose we shall examine the formulas of Stauffer and Reiss for the nucleation rate.

3.1   Kinetic equation

Consider the binary case. Introduce the Reiss' variables x, y as the variables when the free energy in the critical region has the form

$$F = F_c - x^2 + y^2,$$

where F_c is the free energy in the saddle point. These variables can be obtained from ν_1, ν_2 by rotation and rescaling[4].

Instead of rotation and rescaling it is more convenient to introduce the separated variables directly. The variables κ, ξ are the stable and unstable ones. One can come to

$$\frac{\partial^2 F}{\partial \xi \partial \kappa} = -\frac{db_g(\xi)}{d\xi},$$

which is vanished in the saddle point. It means that the square form of the free energy in κ, ξ variables looks like

$$F = -A(\kappa - \kappa_c)^2 + B(\xi - \xi_c)^2 + F_c$$

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[4] May be some part of the Lorenz transformation with an arbitrary parameter has been made. So, these variables aren't completely fixed.

without the cross term. Here A and B are some positive constants

$$A = -(\frac{\partial^2 F(\kappa, \xi)}{2\partial \kappa^2})_c \quad B = (\frac{\partial^2 F(\kappa, \xi)}{2\partial \xi^2})_c$$

Then in the coordinates

$$\tilde{x} = \sqrt{A}(\kappa - \kappa_c) \quad \tilde{y} = \sqrt{B}(\xi - \xi_c)$$

one gets

$$F = F_c - \tilde{x}^2 + \tilde{y}^2$$

Now we shall seek for the similar variables obtained by the linear transformations.

The variables x, y can be obtained from ν_1, ν_2 by the linear transformation

$$x = c_{11}(\nu_1 - \nu_{1c}) + c_{12}(\nu_2 - \nu_{2c}),$$

$$y = c_{21}(\nu_1 - \nu_{1c}) + c_{22}(\nu_2 - \nu_{2c})$$

(which isn't orthogonal) with the known coefficients

$$c_{11} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial \kappa^2})_c]^{1/2}(\frac{\partial \kappa}{\partial \nu_1})_c,$$

$$c_{12} = [-\frac{1}{2}(\frac{\partial^2 F}{\partial \kappa^2})_c]^{1/2}(\frac{\partial \kappa}{\partial \nu_2})_c,$$

$$c_{21} = [\frac{1}{2}(\frac{\partial^2 F}{\partial \xi^2})_c]^{1/2}(\frac{\partial \xi}{\partial \nu_1})_c,$$

$$c_{22} = [\frac{1}{2}(\frac{\partial^2 F}{\partial \xi^2})_c]^{1/2}(\frac{\partial \xi}{\partial \nu_2})_c.$$

The variables x, y practically coincide with $\tilde{x}$, $\tilde{y}$. The difference has an order of a small parameter.

The estimates for coefficients $c_{11}, c_{21}, c_{12}, c_{22}$ are

$$c_{11} \sim \kappa_c^{-2/3},$$

$$c_{12} \sim \kappa_c^{-2/3},$$

$$c_{21} \sim \kappa_c^{-1/2},$$

$$c_{22} \sim \kappa_c^{-1/2}.$$

The estimates

$$\Delta\kappa \sim \kappa^{2/3} \sim \nu_{tot}^{2/3} \sim \Delta\nu_{par}$$

$$\Delta\nu_{perp\ i} \sim \kappa^{1/2} \sim \nu_{tot}^{1/2}$$

in positive powers of a big parameter κ (or ν_{tot}) allows to use the Fokker-Planck's approximation.

In the Fokker-Planck's approximation the kinetic equation for the distribution function n can be written in the following form

$$\partial_t n(\nu_1, \nu_2) = W_1 \partial_1 [n\partial_1 F + \partial_1 n] + W_2 \partial_2 [n\partial_2 F + \partial_2 n],$$

where W_1, W_2 are the kinetic coefficients, i.e. the numbers of the first sort molecules and the second sort molecules which are absorbed by the embryo in the unit of time. Here

$$\partial_1 \equiv \partial/\partial\nu_1, \qquad \partial_2 \equiv \partial/\partial\nu_2$$

and $\partial_t \equiv \partial/\partial t$. The differentiation on the number of the molecules of the given sort in marked by the index near the symbol of the partial differentiation.

Now we rewrite the kinetic equation in the variables x, y. Note that

$$\partial_1 = c_{11}\partial_x + c_{21}\partial_y$$

$$\partial_2 = c_{12}\partial_x + c_{22}\partial_y$$

where $\partial_x = \partial/\partial x$ and $\partial_y = \partial/\partial y$.

The distribution $n(x, y)$ is proportional to the distribution $n(\nu_1, \nu_2)$ with coefficient $\partial(\nu_1, \nu_2)/\partial(x, y)$ and one has to take this difference into account in final calculations. In the near-critical region the coefficients of kinetic equation are approximately constants.

To simplify the treatment one can use notations

$$\partial_{x1} = c_{11}\partial_x, \quad \partial_{x2} = c_{12}\partial_x, \quad \partial_{y1} = c_{21}\partial_y, \quad \partial_{y2} = c_{22}\partial_y.$$

Then one can get the equation

$$\partial_t n = W_1(\partial_{x1} + \partial_{y1})[n(\partial_{x1} + \partial_{y1})F + (\partial_{x1} + \partial_{y1})n]$$
$$+W_2(\partial_{x2} + \partial_{y2})[n(\partial_{x2} + \partial_{y2})F + (\partial_{x2} + \partial_{y2})n]$$

31

Since the structure of terms like $n(\partial_{x1} + \partial_{y1})F$ coincide with the structure of $(\partial_{x1} + \partial_{y1})n$ one can simply miss the last term and reconstruct it in the final expressions. Then

$$\partial_t n = K_1 \partial_x (n \partial_x F + \partial_x n) + K_2 [\partial_x (n \partial_y F + \partial_y n) + \partial_y (n \partial_x F + \partial_x n)] + K_3 \partial_y (n \partial_y F + \partial_y n)$$

where

$$K_1 = W_1 c_{11}^2 + W_2 c_{12}^2$$

$$K_2 = W_1 c_{11} c_{21} + W_2 c_{12} c_{22}$$

$$K_3 = W_1 c_{21}^2 + W_2 c_{22}^2$$

To stress the hierarchy one can introduce the coefficients

$$R = K_1, \quad k = -\frac{K_1}{K_2}, \quad q = \frac{K_3 K_1}{K_2^2}$$

Then finally

$$\partial_t n(\nu_1, \nu_2) = R[\partial_x [n \partial_x F + \partial_x n] - k^{-1} [\partial_x [n \partial_y F + \partial_y n] + \partial_y [n \partial_x F + \partial_x n]]$$

$$+ k^{-2} q \partial_y [n \partial_y F + \partial_y n]]$$

For R, k, q one can get the following expressions

$$R = W_1 c_{11}^2 + W_2 c_{12}^2,$$

$$k = -\frac{W_1 c_{11}^2 + W_2 c_{12}^2}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}},$$

$$q = \frac{(W_1 c_{21}^2 + W_2 c_{22}^2)(W_1 c_{11}^2 + W_2 c_{12}^2)}{(W_1 c_{11} c_{21} + W_2 c_{12} c_{22})^2}$$

The last coefficient can be also written as

$$q = 1 + W_1 W_2 \left(\frac{c_{11} c_{22} - c_{12} c_{21}}{W_1 c_{11} c_{21} + W_2 c_{12} c_{22}}\right)^2.$$

The value of R isn't important because it can be changed by the time rescaling. One can see the estimate

$$k \sim \nu_c^{-1/6}$$

which shows that k is a small parameter. The scale of q is arbitrary, but one can outline situations where $q - 1 \ll 1$.

The boundary conditions for the last equations are the following

$$n/n^e = 1 \qquad x \ll -1 \qquad -\infty < y < \infty,$$

$$\tag{8}$$

$$n/n^e = 0 \qquad x \gg 1 \qquad -\infty < y < \infty$$

The plausible but not rigorous consideration corresponding to the solution proposed by Reiss is the following one

- The main operator of kinetic equation is the last term in r.h.s.

- It ensures the relaxation over the stable variable and the kinetic equation becomes the one dimensional one.

- The consideration of the evolution only over the unstable variable leads to the reduction of the kinetic equation to

$$\partial_t n(\nu_1, \nu_2) = R\partial_x[n\partial_x F + \partial_x n]$$

The solution of the last equation leads to the results of Reiss. But in the cited paper of Reiss the hierarchy was not observed. Hence, the analysis there was less plausible.

3.2 The influence on the characteristics of the process

One needs the transformation of kinetic equation which conserves the boundary conditions, since the variables in the boundary conditions (8) are already separated. This transformation is the Lorenz' transformation.

Introduce the Lorenz' transformation via formulas

$$\psi = \frac{x + \alpha y}{\sqrt{1 - \alpha^2}}, \qquad \eta = \frac{y + \alpha x}{\sqrt{1 - \alpha^2}}$$

This transformation conserves the form of the free energy in the critical region:

$$F = F_c - \psi^2 + \eta^2$$

The kinetic equation is transformed to

$$\partial_t n(\nu_1, \nu_2) = R(1 - \alpha^2)^{-1}k^{-2}[[(k - \alpha)^2 + \alpha^2(q - 1)]\partial_\psi[n\partial_\psi F + \partial_\psi n] -$$

33

$$[(k - \alpha)(1 - k\alpha) - \alpha(q - 1)][\partial_\psi[n\partial_\eta F + \partial_\eta n] +$$
$$\partial_\eta[n\partial_\psi F + \partial_\psi n]] + [(1 - k\alpha)^2 + q - 1]\partial_\eta[n\partial_\eta F + \partial_\eta n]].$$

Parameter α which has the absolute value less than 1 has to be chosen to vanish the cross term. The equation for the choice of α is the following

$$(k - \alpha)(1 - k\alpha) = \alpha(q - 1)$$

Then

$$\partial_t n(\nu_1, \nu_2) = A\partial_\psi[n\partial_\psi F + \partial_\psi n] + C\partial_\eta[n\partial_\eta F + \partial_\eta n]$$

where

$$A = \frac{R}{k^2}(1 - \alpha^2)^{-1}[(k - \alpha)^2 + \alpha(k - \alpha)(1 - k\alpha)]$$

$$C = \frac{R}{k^2}(1 - \alpha^2)^{-1}[(1 - k\alpha)^2 + \frac{(k - \alpha)(1 - k\alpha)}{\alpha}]$$

The parameter of the Lorenz' transformation is given by

$$\alpha = \frac{1}{2k}[k^2 + q - \sqrt{(k^2 + q)^2 - 4k^2}].$$

After the decomposition at small k one can come to

$$\alpha = \frac{1}{q}k. \tag{9}$$

in the leading term. One can see that it is small. So, it is difficult to see the effect of the Stauffer's consideration on the direction of the flow. But one can not directly put $\alpha = 0$ because there is a small parameter k. Expression for A will be

$$A = R\frac{q - 1}{q}. \tag{10}$$

The ratio $1/q$ is not small. So the correction to the Reiss' formula is essential. The direct substitution $\alpha = 0$ leads to

$$A|_{\alpha=0} = R$$

which is the Reiss' result and it is not precise.

3.3 Some consequences for the binary nucleation

The question to discuss here is the rate of the deviation of the Reiss' formula for the nucleation rate from the analogous result of Stauffer.

In the derivation of the expression for q no suppositions about W_1 and W_2 have been made. At first the situation with the moderate ratio W_1/W_2 will be discussed.

As far as

$$\frac{\partial \xi}{\partial \nu_1} = \frac{\partial (1 - \xi)}{\partial \nu_2} = -\frac{\partial \xi}{\partial \nu_2} \tag{11}$$

we see that the partial cancellation can take place in expression for q only in

$$W_1 c_{11} c_{21} + W_2 c_{12} c_{22}$$

but not in

$$c_{11} c_{22} - c_{12} c_{21}$$

So q is big enough to lead to result near the Reiss' formula $A = R$. This shows that the Reiss' formula is not so bad although it is not a true result.

The precise coincidence of Reiss' and Stauffer's results takes place when $q = \infty$, i.e. when

$$W_1 c_{11} c_{21} + W_2 c_{12} c_{22} = 0$$

The last relation taking into account (11) can be rewritten as

$$W_1 \frac{\partial \kappa}{\partial \nu_1} = W_2 \frac{\partial \kappa}{\partial \nu_2}$$

In the rough approximation corresponding to:

- the capillary approximation itself,

- the Gibbs-Duhem' equation in the capillary approximation

- the negligible dependence of v_i on κ in capillary approximation

one can see that the last relation transforms to

$$W_1 v_1 = W_2 v_2$$

where v_i is the volume per molecule in a liquid phase. This condition is the condition of precise applicability of the Reiss' result. It differs from condition

$$W_1 = W_2$$

announced in paper [10] analyzing the theory of Stauffer.

It is clear that the last condition is wrong which opens a question of the formal validity of the Stauffer's derivation. Really, formally regarding one molecule of the first substance as several particles, one can attain the applicability of Reiss' result by such an artificial way. For condition $W_1 v_1 = W_2 v_2$, this trick fails.

Let us extract the conditions when A essentially differs from R. It can be only when

$$q \approx 1$$

The last condition can be satisfied only when $W_1 \ll W_2$, $W_1 \gg W_2$. Namely, this situation occurs when there is the rapid component. *The essential variation of the nucleation rate in comparison with the Reiss' formula is possible only under the hierarchy of the kinetic coefficients.* This situation requires a separate analysis.

As an illustration here we shall show the result in a square approximation of the free energy, although one can analytically prove that the existence of a rapid component throws the main nucleation flow away from the near-critical region and another approximations for the free energy have to be used.

Under the hierarchy one can see the evident rapid component and formulas can be simplified. The simplification can be made also directly in the final formulas and the expression for A

$$A = W_2 \frac{(c_{11} c_{22} - c_{12} c_{21})^2}{c_{21}^2}$$

is proportional to W_2. Then

$$A = W_2 \left(-\frac{1}{2} \frac{\partial^2 F}{\partial \kappa^2} \right) \left[\frac{\partial \kappa}{\partial \nu_1} + \frac{\partial \kappa}{\partial \nu_2} \right]^2$$

In the further considerations of this section this simplification is not used.

3.4   Conclusions based on hierarchy

In the post critical region one can assume the derivative on the unstable variable to be locally a constant and reduce the kinetic equation to

$$\partial_t n = R[\partial_x(\partial_x + h) - k^{-1}(\partial_x(\partial_y + 2y) + \partial_y(\partial_x + h)) + k^{-2} q \partial_y(\partial_y + 2y)]n,$$

where h is the constant coefficient corresponding to the first derivative on the unstable variable and the values of R,k, q are changed since the derivatives are taken now in the local current point. Renormalize the scale over the unstable variable as to put $h = 1$. Certainly, the hierarchy takes place after the renormalization.

We are interested in the stationary solution and shall seek it in the form

$$n = Q(x) \exp(-(y - y_0)^2) \qquad (12)$$

with the constant mean value y_0 and some function $Q(x)$. The derivative $dQ(x)/dx$ can be neglected. Then

$$[-k\partial_y h + q\partial_y(\partial_y + 2y)]n = 0$$

For y_0 one can get taking into account

$$\partial_y \exp(-(y - y_0)^2) = -2(y - y_0) \exp(-(y - y_0)^2),$$

$$\partial_y(\partial_y + 2y) \exp(-(y - y_0)^2) = -4y_0(y - y_0) \exp(-(y - y_0)^2)$$

the following relation

$$\frac{kh}{q} = 2y_0. \qquad (13)$$

So the solution is obtained.

Consider this solution. We see that the deviation of the rapid parameter is small also in the post critical region and the possible hidden parameter can not be extracted.

Due to the slope of the free energy surface on κ the minimum of the free energy in the cross section depends on the slope of this cross section. But since the slope of the free energy surface on κ is small the deviation of the minimum is small also. This deviation can be considered as the deviation of the mean value of the rapid variable and leads to the absence of the possibility to extract this variable in the post critical region also.

The analogous method can be applied also for the near-critical region. In the near-critical region one can make the substitution

$$n = P(x) \exp(-(y - y_0(x))^2),$$

where y_0 is now the function of x. One can determine y_0 according to

$$(\partial_x - 2x)n = -J_x,$$

there the r.h.s. is constant. Then

$$\partial_x n = -J_x + 2xn. \tag{14}$$

The linear character of the last equation ensures the linear dependence of y_0 on the unstable variable. As far as the flow is reciprocal to the halfwidht (along the trajectory y_0) one can get the equation on the flow. The linear dependence of y_0 on x ensure the linear character of the transformation which is analogous to the Lorenz' transformation.

This way of considerations can be applied to the more general situations without the square form of the free energy. Then the trajectory isn't the straight line and the solution is some approximation based on the hierarchy.

The last question to solve is a real position of the near-critical region.

When the deviation of the flow from the steepens descent situation is essential there is the danger to violate the square form of the free energy. The boundary conditions for kinetic equation in the critical region in reality have to be observed at

$$n/n^e = 1 \quad x \sim -1 \quad -1 < y < 1,$$

$$n/n^e = 0 \quad x \sim 1 \quad -1 < y < 1.$$

After the Lorenz' transformation

$$n/n^e = 1 \quad \psi \sim -1 \quad -1 < \eta < 1,$$

$$n/n^e = 0 \quad \psi \sim 1 \quad -1 < \eta < 1.$$

Rigorously speaking one has to put the equilibrium conditions at the line where $F = F_c - 1$ which is invariant to Lorenz' transformation. But actually, to ensure the finite relaxation time and the constant values of kinetic coefficients one has to cut-off the tails and to go to the boundary of the reduced near-critical region. But this boundary is not invariant to Lorenz' transformation.

The last definition of the boundary conditions has to be considered as the main one.

But here the reduced near-critical region is stretched along one of the lines $F = F_c$ where the transition occurs. The square approximation in such stretched region can be invalid.

3.5 Conclusions

The main new results of the consideration made above are the following:

- The hierarchy of terms in kinetic equation is shown. Earlier the hierarchy was observed only for halfwidths of the near critical region [25].

- The plausible way to derive the Reiss' formula was demonstrated. Since this formula is wrong, this deviation demonstrates the impossibility to neglect in kinetic equation all terms except the main one.

- The moderate value of the error made by Reiss is established. Earlier there was a strong conviction that the error of the Reiss' approach can be enormous, which was illustrated by numerical examples in [6]. Now it is clear that the big error can be only in the cases of strong hierarchy between kinetic coefficients ($W_1 \gg W_2, W_2 \gg W_1$) when the nucleation flux goes mainly far from the saddle point.

- The simplified relations for α (see (9)) and for the nucleation rate (see equation (10) for A) have been derived.

- The super-critical region is studied and the expression for the distribution function over the stable variable (12), (13) in this region is derived.

One can see that the precise result is rather complex. It can not be achieved by a simple superposition of naive solutions based on hierarchy. One has also to mention that even in hierarchy $W_1 \gg W_2$ the result differs from the naive one.

But the main result is the absence of the really important corrections in comparison with a naive approach. All obtained corrections are rather small and mainly less than the microscopic corrections in real situations. Below, we shall seek essential corrections in the case of hierarchy.

4 Nucleation rate in the situation with hierarchy

The case of hierarchy certainly requires a special consideration going outside the local approximations in the neighborhood of a saddle point of the embryos free energy.

There are many substances for which the densities $n_{\infty i}$ have the different orders of the values. For example,

$$\frac{n_{\infty H_2O}}{n_{\infty H_2SO_4}} > 10^5$$

in the everyday thermodynamic conditions.

Assume that there are two groups of substances: the substances with a slow exchange and the substances with a rapid exchange. Suppose

$$W_a^+ \ll W_b^+$$

The components of the first group will be marked by the index "a" and the components of the second group will be marked by the index "b". At first we shall consider the situation of two components and later the generalization will be evident.

Here the variable $\tilde{v}$ is the following one

$$\tilde{v} = \sum_a v_{la} \nu_a \quad . \tag{15}$$

4.1 Direction of a flow

Extract the conditions when the flow is parallel to ν_b. We construct a simple model which will show some estimates.

The quantity of the embryos at the bottom with a fixed slow component can be estimated from above by

$$N_{above} = \Delta \nu n_0 \exp(-F_b)$$

where F_b is the free energy at the bottom $\Delta \nu$ is the effective width of the bottom. The normalizing factor n_0 in some situations of the overcoming of the few activation barriers can differ from the standard one. That's why we keep a special definition for this factor.

The quantity of the embryos in the critical region which change the number ν_a in the unit of time is

$$I_A = W_a^+ \Delta \nu n_0 \exp(-F_b)$$

The flow over the ridge is J_s. So, the necessary condition is the following

$$W_a^+ \Delta \nu n_0 \exp(-F_b) \ll J_s \quad . \tag{16}$$

One can adopt for J_s the following expression

$$J_{sb} = W_b^+ n_0 \exp(-F_t)/\Delta\nu\pi^{1/2} \tag{17}$$

where F_t is the free energy at the top of the ridge and put $\Delta\nu$ as

$$\Delta\nu = \left(\frac{\partial^2 F(\nu_a, \nu_b)}{2\partial\nu_b^2}\right)^{-1/2}\big|_{\nu_a=\nu_{ac}, \nu_b=\nu_{bc}} \quad. \tag{18}$$

It is necessary that the transition occurs earlier than the near-critical region is attained. Then it is possible to put

$$F_b = F_c - 1$$

at the boundary of the near-critical region. At the same boundary one can also put

$$F_t = F_c + 1$$

The inequality (16) comes to

$$W_a^+ \ll \frac{W_b^+}{\exp(2)(\Delta\nu)^2\pi^{1/2}} \quad. \tag{19}$$

Practically the same condition can be obtained by the comparison of the characteristic time between the transitions of the embryo along ν_a which is

$$t_{tr} \sim (W_a^+)^{-1}$$

and the time of the relaxation in the bottom

$$t^s = \frac{(\Delta\nu_b)^2}{W_b^+} \quad.$$

4.2   The normalizing factor

Here we shall see that there is no equilibrium distribution in the whole pre-critical region.

Extract the condition when there will be the equilibrium distribution at the level with the fixed ν_a of the pre-critical region. The quasi equilibrium distribution has the form

$$n = n^q = n_0^q \exp(-F(\nu_a, \nu_b))|_{\nu_a=const} \quad. \tag{20}$$

41

The normalizing factor n_0^q differs from the standard normalizing factor because there is an equilibrium along the band but there is no equilibrium between bands.

To establish the equilibrium it is sufficient to have the intensity of the contact between the neighbor bands greater than the intensity of the overcoming over the activation barrier. So, it is necessary to determine the height of the activation barrier. Choose as ν_b the value of ν_{be}, corresponding to the minimum of the free energy at the band

$$\nu_{be} \ : \ min_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_b) \ . \qquad (21)$$

Then the intensity of the contact can be estimated by $W_a^+ n_0 \exp(-F(\nu_a, \nu_{be})$.

One can due to (19) assume that the transition to the post critical region occurs along ν_b, i.e. inside the band[5]. Beside ν_{be} one can introduce ν_{bx} as the point inside the band where the free energy has the maximum

$$max_{\nu_b} F(\nu_a, \nu_b) = F(\nu_a, \nu_{bx}) \equiv F_x(\nu_a) \ . \qquad (22)$$

Under the square approximation the transition along ν_b can not occur because this variable is the stable one. Then $\nu_b{}_x$ can not be defined. But if the component ν_b is supersaturated over the pure plane liquid then the condensation into the pure liquid is possible and $\nu_b{}_x$ must exist. This shows that the square approximation can not be used here.

The transition into the super critical region can occur under the arbitrary ν_a. But the probability of such transition is very low for all ν_a when $\exp(-F_x(\nu_a))$ strongly differs from $\exp(-F_c)$, i.e. out of the critical region. But it can be greater than the intensity to come to the next band. The intensity of the establishing of the equilibrium (not the quasi equilibrium) at the next band[6] is less than the intensity of the transition over the ridge. This intensity is given by

$$J = J_s = n_0^q \exp(-F_x(\nu_a)) W_{bx}^+ / \Delta_x \nu_b \pi^2 \ , \qquad (23)$$

where

$$W_{bx}^+ = W_b^+(\nu_a, \nu_{bx}); \quad \Delta_x \nu_b = \left(\frac{\partial^2 F(\nu_a, \nu_b)}{2\partial\nu_b^2}\right)^{-1/2}\Big|_{\nu_b=\nu_{bx}} \ . \qquad (24)$$

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[5] The value $\Delta\nu_b$ depends on ν_a weakly.
[6] The intensity of transition to the next band.

There is no need to establish the equilibrium along the whole band with the small ν_a. The value of ν_{bx} for small ν_a can be very big, the barriers of the nucleation can be very high, but it is necessary to have the equilibrium only near the bottom, i.e. at ν_b near to ν_{be}. The establishing of the equilibrium along the whole pre-critical region of the band is necessary only for the bands where the intensity of the transition to the post critical region is essential (comparable with the intensity of the transition between the bands). According to the previous considerations there is the quasi equilibrium along such bands.

Introduce the number of embryos in the band

$$N(\nu_a) = n_0^q \exp(-F(\nu_a, \nu_{b\ e}))\Delta_e\nu_b \quad , \tag{25}$$

where

$$\Delta_e\nu_b = \sum_{\nu_b=0}^{\nu_{bx}} \exp(-F(\nu_a, \nu_b) + F(\nu_a, \nu_{be})) \tag{26}$$

has a sense of characteristic width. The last formula in a continuous limit can be transformed to

$$\Delta_e\nu_b = \int_0^{\nu_{bx}} \exp(-F(\nu_a, \nu_b) + F(\nu_a, \nu_{be}))d\nu_b \quad . \tag{27}$$

At the ends of the interval of integration the equilibrium distribution can be violated but there the subintegral function goes to zero. As far as $\exp(-F)$ as function of ν_b is rather sharp near the maximum then the number of the embryos going from the band with ν_a to the band with $\nu_a - 1$ can be approximated by $W_a^-(\nu_a, \nu_{be})N(\nu_a)$. The number of the forward transitions is $W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1)$. Then one can write the balance equation at the band

$$\frac{\partial N}{\partial t} = W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1) + W_a^-(\nu_a + 1, \nu_{be})N(\nu_a + 1) -$$

$$\tag{28}$$

$$W_a^+(\nu_a, \nu_{be})N(\nu_a) - W_a^-(\nu_a, \nu_{be})N(\nu_a) - J(\nu_a) \quad .$$

For $J(\nu_a)$ one can get

$$J(\nu_a) = N\frac{W_{bx}^+ \exp(F(\nu_a, \nu_{be}) - F_x(\nu_a))}{\Delta_e\nu_b\Delta_x\nu_b} \quad . \tag{29}$$

One can see that the absence of the equilibrium distribution in the whole pre-critical region is the characteristic feature of the transition far from the saddle point.

4.3   Valley zone and ridge zone

For every ν_a in the pre-critical region there will be ν_{be}. The curve $\nu_{be}(\nu_a)$ will be called the valley in ν_a, ν_b plane.

For every ν_a in the region under consideration there will be ν_{bx}. The curve $\nu_{bx}(\nu_a)$ will be called the ridge in ν_a, ν_b plane.

Since there is a slope of the ridge and the valley in ν_a direction it is necessary to specify the set of variables.

In the set of variables κ, ξ the channel of nucleation is the straight analog of a valley. But the channel of nucleation does not coincide with the the valley in ν_a, ν_b plane.

The line analogous to the ridge, i.e. the ridge in κ, ξ plane will be the separation line defined as

$$\frac{\partial F(\kappa, \xi)}{\partial \xi} = 0$$

$$\frac{\partial F(\kappa, \xi)}{\partial \xi} < 0$$

The values at the channel of nucleation here will be marked by the subscript h and at the separation line the values will be marked by the subscript s.

We see that effectively the flow is directed along ν_b. The problem to get $J(\nu_a)$ is purely a one dimensional problem. So, in the band $\nu_a = const$ there exists the valley $\nu_b \approx \nu_{b\,e}$ zone and the ridge $\nu_b \approx \nu_{b\,x}$ zone. Precise definitions are the following

- The ridge zone in ν_b scale is determined by conditions

$$F(\nu_a, \nu_b) \geq F(\nu_a, \nu_{bx}) - 1$$

Certainly, $F(\nu_a, \nu_b) \leq F(\nu_a, \nu_{bx})$. This zone has to be near the given ridge.

- The valley zone in ν_b scale is determined by conditions

$$F(\nu_a, \nu_b) \leq F(\nu_a, \nu_{be}) + 1$$

Certainly, $F(\nu_a, \nu_b) \geq F(\nu_a, \nu_{be})$. This zone has to be near the given valley.

To find the value of the flow $J(\nu_a)$ one has to solve kinetic equation in the ridge zone. To find the normalizing factor like it was done in heterogeneous nucleation it is necessary to consider the valley zone and to solve kinetic equation in this region.

The problem under consideration is the influence of the surface excesses on the forms of the free energy in the ridge zone and the valley zone. Fortunately some simplifying properties will be established below which help to escape from the explicit inclusion of surface excesses in the kinetic equation.

For the ridge zone these properties are the following

- Define by the subscript 0 the values without surface excesses

- In the ridge zone for arbitrary s corresponding to the ridge zone

$$F(\nu_a, \nu_{bx} + s) - F(\nu_a, \nu_{bx}) \approx F(\nu_a, \nu_{bx0} + s) - F(\nu_a, \nu_{bx0})$$

For the valley zone these properties are the following

- In the valley zone for arbitrary s corresponding to the valley zone

$$F(\nu_a, \nu_{be} + s) - F(\nu_a, \nu_{be}) \approx F(\nu_a, \nu_{be0} + s) - F(\nu_a, \nu_{be0})$$

One can analogously define the channel zone and the separation zone.

- The separation zone is determined by conditions

$$F(\kappa, \xi) \geq F(\kappa, \xi_s) - 1$$

The value of κ is fixed here. Certainly, $F(\kappa, \xi) \leq F(\kappa, \xi_s)$. The separation zone has to be near the given separation line.

- The channel zone is determined by conditions

$$F(\kappa, \xi) \leq F(\kappa, \xi_h) + 1$$

The value of κ is fixed here. Certainly, $F(\kappa, \xi) \geq F(\kappa, \xi_h)$. The channel zone has to be near the given channel line.

One can analytically prove the following properties for the separation zone

45

- In the separation zone for arbitrary s corresponding to the separation zone

$$F(\kappa, \xi_s + s) - F(\kappa, \xi_s) \approx F(\kappa, \xi_{s0} + s) - F(\kappa, \xi_{s0})$$

One can analytically prove the following properties for the channel zone

- In the channel zone for arbitrary s corresponding to the channel zone

$$F(\kappa, \xi_h + s) - F(\kappa, \xi_h) \approx F(\kappa, \xi_{h0} + s) - F(\kappa, \xi_{h0})$$

The method of a proof of all these properties is quite analogous to the already presented for the near-critical region. These properties allow to solve kinetic equations in these regions by some shift renormalizations and solutions in the absence of the the surface excesses.

4.4 Discrete case

Consider the stationary solution. The last equations form the system of algebraic equations. Note that the sufficient equations are those where $W_a^+ N$ has the order of J. The equations with $W_a^+ N \gg J$ can be taken into account by the boundary condition $n = n^q = n^e$ for ν_a which is less than some ν_{amin}, where J begins to be comparable with $W_a^+ N$. More precisely this question will be discussed later.

Formally one has to put this condition at $\nu \ll \nu_{amin}$. Then one has to solve equations and to see where the condition $n \approx n^e$ will be violated. It is very easy to do having calculated $J(\nu_a)$ on the base of n^e to get

$$n \approx n^e - \int_{-\infty}^{\nu_a} J(\nu_a')d\nu_a'$$

or having expelled the unphysical region

$$n \approx n^e - \int_{1}^{\nu_a} J(\nu_a')d\nu_a'$$

This will give the necessary estimate.

In the region where $W_a^+ N \ll J$ the solution is rather simple

$$n \ll n^e \quad . \tag{30}$$

This condition will be seen automatically at some ν_a and since n/n^e is a decreasing function of ν_a it will take place later. So, one has to investigate only few equations of the type

$$W_a^+(\nu_a - 1, \nu_{be})N(\nu_a - 1) + W_a^-(\nu_a + 1, \nu_{be})N(\nu_a + 1)$$

$$-W_a^+(\nu_a, \nu_{be})N(\nu_a) - W_a^-(\nu_a, \nu_{be})N(\nu_a) = J(\nu_a) \quad . \tag{31}$$

The total flow is defined as

$$J_{int} = \sum_{\nu_a = \nu_{amin}}^{\nu_{amax}} J(\nu_a) \quad , \tag{32}$$

where ν_{amax} marks the upper boundary of the equations sufficient for the consideration.

In the limit when there is only one sufficient equation[7]

$$J_{int} = W_a^+ \int_0^{\nu_{bx}} n_0 \exp(-F(\nu_a, \nu_b))d\nu_b \quad = W_a^+ N_{tot}(\nu_a) \tag{33}$$

where the total number of droplets at ν_a is

$$N_{tot}(\nu_a) = \int_0^{\nu_{bx}} n_0 \exp(-F(\nu_a, \nu_b))d\nu_b$$

The discrete situation is the most frequent one. But namely this situation has not been considered earlier.

4.5 Differential model

Consider the opposite situation when among (31) there are so many equations that it is difficult to solve the algebraic equations. Then it is reasonable to come to the differential form. The condition of the validity of the differential form coincides with the condition of the big number of the essential equations. Then

$$J(\nu_a) = -\frac{\partial}{\partial \nu_a}\{(W_a^+(\nu_a, \nu_{be}) - W_a^-(\nu_a, \nu_{be}))N(\nu_a)\} +$$

$$\frac{\partial^2}{2\partial \nu_a^2}\{(W_a^+(\nu_a, \nu_{be}) + W_a^-(\nu_a, \nu_{be}))N(\nu_a)\} \quad . \tag{34}$$

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[7] Having attained ν_a all embryos come automatically to the super critical region. Then it is possible to write the expression for the transition on ν_b.

With account of (29) one can get

$$N\frac{\exp(F(\nu_a, \nu_{be}) - F_x(\nu_a))}{\Delta_e\nu_b\Delta_x\nu_b}W_{bx}^+ =$$
$$\frac{\partial}{\partial\nu_a}\{(W_a^+(\nu_a, \nu_{be})(1 - \exp(\frac{\partial F(\nu_a, \nu_{be})}{\partial\nu_a})))N(\nu_a)\} + \qquad (35)$$
$$\frac{\partial^2}{2\partial\nu_a^2}\{(W_a^+(\nu_a, \nu_{be})(1 + \exp(\frac{\partial F(\nu_a, \nu_{be})}{\partial\nu_a})))N(\nu_a)\} \quad .$$

One can note that

- The hierarchy of the halfwidths of the near-critical region shows that the quasi-unary nucleation in the square approximation in the neighborhood of the saddle point is impossible.

So, the change of approximation to a linear one is absolutely necessary. This conclusion is very essential for further consideration.

One can use the following approximations

$$J = J_0 \exp(cy) \quad , \qquad (36)$$

$$y = \nu_a - \nu_{a0} \quad , \qquad (37)$$

$$c = \frac{\partial F(\nu_a, \nu_{be})}{\partial\nu_a}|_{\nu_a=\nu_{a0}} - \frac{\partial F(\nu_a, \nu_{bx})}{\partial\nu_a}|_{\nu_a=\nu_{a0}} \quad , \qquad (38)$$

$$J_0 = J(\nu_a)|_{\nu_a=\nu_{a0}} \quad . \qquad (39)$$

It means that the linear approximation for $F(\nu_a, \nu_{bx}) - F(\nu_a, \nu_{be})$ is adopted. The supposition made in this paper radically changes from the supposition of Trinkaus. This difference will be discussed in a special part of this paper.

One has to note that

$$\frac{\partial F(\nu_a, \nu_{be})}{\partial\nu_a}$$

differs from

$$\frac{\partial F(\nu_a, \nu_b)}{\partial\nu_a}$$

and

$$\frac{\partial F(\nu_a, \nu_{bx})}{\partial\nu_a}$$

differs from

$$\frac{\partial F(\nu_a, \nu_b)}{\partial \nu_a} \quad .$$

When we use $\frac{\partial F(\nu_a, \nu_{be})}{\partial \nu_a}$ we imply the differentiation along the bottom of a valley. When we use $\frac{\partial F(\nu_a, \nu_{bx})}{\partial \nu_a}$ we imply the differentiation along the top of a ridge.

Then one can get

$$I \exp(cy)N = -W_a^+(1-\epsilon)\frac{dN}{dy} + W_a^+(1+\epsilon)\frac{d^2N}{2dy^2} \quad , \tag{40}$$

where

$$I = \frac{W_{bx}^+ \exp(F(\nu_{a0}, \nu_{be}) - F_x(\nu_{a0}))}{\Delta_e \nu_b \Delta_x \nu_b} \quad , \tag{41}$$

$$W_a^+ = W_a^+(\nu_a, \nu_{be}) \quad , \tag{42}$$

$$\epsilon = \exp\left(\frac{\partial F(\nu_a, \nu_{be})}{\partial \nu_a}\right) \quad . \tag{43}$$

It is supposed that ϵ depends on ν_a rather weakly. We suppose that ϵ is locally a constant value. This supposition is many times weaker than the previous approximation.

Since $\frac{\partial F(\nu_a, \nu_{be})}{\partial \nu_a}$ is small the value of ϵ is close to 1 and $1 - \epsilon$ is very small. Then the value $1 + \epsilon$ is close to 2. Then the relative deviation of $\frac{\partial F(\nu_a, \nu_{be})}{\partial \nu_a}$ have no importance.

Then one can get

$$x = cy \quad , \quad N\exp(x) + A\frac{d^2N}{dx^2} + B\frac{dN}{dx} = 0 \tag{44}$$

with the known values of A, B.

After the transition to $\tilde{\psi} = \exp(x)$ one can get

$$A\tilde{\psi}^2 N'' + (A+B)\tilde{\psi}N' + \tilde{\psi}N = 0 \tag{45}$$

with the known solution

$$N = \tilde{\psi}^{-B/(2A)} Z_{B/A}\left(\frac{2}{\sqrt{A}}\tilde{\psi}^{1/2}\right) \quad , \tag{46}$$

where Z_i is the cylinder function. One has to choose the solution vanishing at ∞.

The known value of N allows to determine the total intensity of the embryo formation and the integral can be taken analytically.

4.6 Applicability of solution

Our solution corresponds to the solution derived by H. Trinkaus in [9]. But this correspondence is only a formal one. Recall the derivation by Trinkaus in [9]. Trinkaus proposed the linearization of the free energy F (G in terms of Trinkaus) around $\hat{n}_2$ (this value is analogous to ν_{a0}).

Now we shall analyze the possibility of linearization of F in the vicinity of ν_{a0}. This linearization can be considered in the global sense and in the local sense when linearization is done over one coordinate while the other coordinate determines the values of coefficients in this linearization.

Linearization in the global sense can not exist because the second derivative at the ridge and the second derivative at the valley must have different values. Only then the value of

$$\Delta F(\nu_a) \equiv F(\nu_a, \nu_{bx}) - F(\nu_a, \nu_{be})$$

will be a real activation barrier. The exponent of the last value is the leading term in the expression for the flow.

Linearization in the local sense can not be valid also. It is absolutely clear that the linearization over ν_b can not be made because it is necessary to have a valley and a ridge for F as a function of ν_b. So, it can not be linearized. Another possibility is to fulfill linearization over ν_a while coefficients depend on ν_b. The last possibility is the most preferable one.

The careful analysis of the last possibility shows the impossibility of linearization. Really, since the ridge in ν_a, ν_b scale is relatively close to the ridge in κ, ξ scale one can see that the behavior of F as a function of ν_a at ν_b slightly greater than ν_{bx} is the following one: At first F increases until the ridge in ν_a, ν_b will be attained. Later with increase of ν_b the value of F will decrease. This behavior is the direct consequence of the slope of the channels of nucleation in ν_a, ν_b plane. So, the linearization is impossible.

The only possible variables, in which the approximate local linearization is valid are variables κ, ξ. One can see that there F can be linearized far from the critical point

$$\partial F(\kappa, \xi)/\partial \kappa = 0$$

at every ξ. The linearization is made only along κ. But these variables have not been even mentioned in [9].

It has been already analytically shown that we are far from the critical point. Namely this allows the linearization in a local sense along κ.

The critical point which is the nearest to the origin of coordinates is situated in the channel in ν_a, ν_b picture. This is the real saddle point. But since we are far from the main saddle point it means that we are far from every critical point.

Now we shall see that the linearization of the free energy in κ, ξ variables is possible. Really,

$$\frac{\partial F(\kappa, \xi)}{\partial \kappa} = -b_g(\xi) + 2\kappa^{-1/3}/3$$

The second derivative is

$$\frac{\partial^2 F(\kappa, \xi)}{\partial \kappa^2} = -2\kappa^{-4/3}/9$$

The size of characteristic region in which the linearization is necessary can be estimated as

$$\Delta\kappa = (b_g(\xi) - 2\kappa^{-1/3}/3)^{-1}$$

So, the necessary condition is

$$|(-b_g(\xi) + 2\kappa^{-1/3}/3)^{-2}2\kappa^{-4/3}/9| \ll 1$$

Since we are far from the critical point one can neglect the compensation in $(-b_g(\xi) + 2\kappa^{-1/3}/3)$ and get

$$|(2\kappa^{-1/3}/3)^{-2}2\kappa^{-4/3}/9| \ll 1$$

or

$$\kappa^{-2/3} \ll 1$$

The last inequality is evident.

The last property is important for our needs. We are interested in the linearization of the free energy of the ridge and of the valley. Really, the particular case of the last derivation is the possibility of linearization of F along the ridge and the valley in κ, ξ scale, i.e. along the channel and along the separation line.

The last step is to go from κ, ξ picture to ν_a, ν_b picture. We see that the slope of the valley and the ridge in κ, ξ picture along κ is very small. Since the slope is proportional to $|\frac{\partial F(\kappa, \xi)}{\partial \kappa}|$ it can be seen from

$$|\frac{\partial F(\kappa, \xi)}{\partial \kappa}| = |-b_g(\xi) + 2\kappa^{-1/3}/3| \sim 2\kappa^{-1/3}/3 \ll 1$$

51

So, the characteristic distance where the height of the valley, the height of the ridge and, thus, the height of the activation barrier (in fact it can be proven that there is no compensation) undergo the variation of one thermal unit is

$$D_1 = \kappa^{1/3}$$

One can see that $D_1 \ll \kappa$ and it means that the relative size of the transition region has to be small.

This slope has to compared with the characteristic halfwidth along ν_b or the characteristic size D_1 has to be compared with the half-width along ξ multiplied on κ. We have

$$D_2 = (\frac{\partial^2 F(\kappa, \xi)}{2\partial \xi^2})^{-1/2} \kappa = (\frac{\partial^2 b_g(\xi)}{2\partial \xi^2})^{-1/2} \kappa^{1/2} \sim \kappa^{1/2}$$

We see that

$$D_2 \ll D_1$$

The slope at the boundary of halfwidth is

$$\frac{\partial^2 F(\kappa, \xi)}{\partial \xi^2} D_2/\kappa \sim \kappa^{1/2}$$

and it is rather essential.

We introduce the distance D_3 where the slope

$$S_l = \frac{\partial^2 F(\kappa, \xi)}{\partial \xi^2} D_3/\kappa^2 \sim D_3/\kappa$$

has to the order of the slope of the ridge $\partial F/\partial \kappa \sim \kappa^{-1/3}$, i.e. $\kappa^{-1/3}$. Then we get

$$D_3 \sim \kappa^{2/3}$$

We see that the order of D_3 is the same as the order of D_1 and it is relatively small

$$D_3 \ll \kappa$$

It means that the deviation of the separation line in κ, ξ scale from the ridge in ν_a, ν_b scale is relatively small.

Since F_h, F_s allow linearization as functions of κ or of ν_a we come to a conclusion that the linearization of F_e, F_r, ΔF (this value is a function of one variable) as a function of κ or of ν_a is quite possible.

4.7   Simplified solution

Since $\partial F(\nu_a, \nu_{be})/\partial \nu_a \ll 1$ one can put $\epsilon = 1$. Then $B = 0$ and one come to the universal solution

$$N \sim Z_0(\frac{2}{\sqrt{A}}\tilde{\psi}^{1/2}) \qquad (47)$$

This is the universal function Z_0 of the variable

$$\frac{2}{\sqrt{A}}\exp(cx/2)$$

Finally we get a universal solution.

4.8   Discussion

The multidimensional case is quite analogous to the two-dimensional one. In the multidimensional nucleation one has to consider some channel of nucleation. One has to extract the set of fast variables $\{\nu_b\}$ and the set of slow variables $\{\nu_a\}$.

For the set $\{\nu_a = fixed\}$ one can establish $J_{\{\nu_a\}}$ by the consideration of the evolution in the set $\{\nu_b\}$. It can be done by the standard methods from the previous sections.

After the calculation of $J_{\{\nu_a\}}$ one can define the direction. It will be the quasi-integral on ν_a. This defines the first coordinate. The second coordinate is the direction of the bottom of the valley in the cross section $\{\nu_b = const\}$. The further consideration is absolutely analogous.

The new results formulated above are the following:

- In the paper of Trinkaus [9] only the differential case was considered. The discrete case was not considered there. Really, the height of the pseudo-activation barrier can change rather rapidly with increase of ν_a. This leads to the preference of discrete model.

  As for the half-widths of the bottom of the channel and of the top of the ridge in calculation of J there are inequalities which guarantee the possibility of the differential description. Really, these half-widths increase like $\kappa^{1/2}$ (see the standard estimates for the half-widths along the stable variables). But if even these variables will be not so big nothing will be changed because they variate slowly in comparison with the exponent of the height of the pseudo-activation barrier. So, the mathematical structure of the balance equation will be the same.

- Here the surface limited growth is considered while in [9] the diffusion limited growth was used. It seems that because the transition occurs earlier than the saddle point will be attained the embryos are small enough and the surface limited growth is preferable.

- It is shown that the absence of the equilibrium distribution in the pre-critical region is the driving force of the transition far from the saddle point. This fact stresses once more the importance of the formulation of the boundary conditions and outlines the paper [8] where the boundary conditions were used for the situation without hierarchy of kinetic coefficients.

- The hierarchy of the halfwidths of the near-critical region (more accurate the near-saddle region) shows that the quasi-unary nucleation in the square approximation in the neighborhood of the saddle point is impossible. So, the change of approximation to a linear one is absolutely necessary. Moreover, it is impossible to see the transition of the Stauffer's solution to Trinkaus' one on the analytic level of explicit formulas.

Beside the mentioned disadvantages of the differential approach one can mention the disadvantage connected with the position of the basic point ν_a^* for decompositions of the height of the ridge and depth of the valley. An ordinary chosen point for such decompositions is

$$W_a^+ = J(\nu_a)/N(\nu_a) \tag{48}$$

The presence of this point awakes the idea of the Genuine Saddle Point [11]. It is reasonable to put the point of decomposition at

$$n(\nu_a^*) = n_{eq}(\nu_a^*)/2 \tag{49}$$

The shift between ν_a^* determined by (48) and (49) will be called "the soft shift".

The greater is $|c|^{-1}$, the greater is the soft shift. But the applicability of differential approach requires

$$|c| \ll 1$$

The last parameter ordinary comes from two decompositions: one of the height of the ridge[8]

$$F_r(\nu_a) = F_r(\nu_{a0}) + k_r(\nu_a - \nu_{a0})$$

---

[8] Take a cross section $\{\nu_b = const\}$.

with parameter k_r and another of the depth of the valley[9]

$$F_e(\nu_a) = F_e(\nu_{a0}) + k_e(\nu_a - \nu_{a0})$$

with parameter k_e.

Ordinary

$$k_e > 0$$

(the opposite sign means that the saddle point is already behind)

$$k_r < 0$$

(the opposite sign means that energetically it was more profitable to cross the ridge earlier[10]). Then in

$$J \simeq J_0 \exp(-k_r(\nu_a - \nu_{a0}) + k_e(\nu_a - \nu_{a0})) = J_0 \exp(c(\nu_a - \nu_{a0}))$$

parameters k_e and k_r can not be compensated. Ordinary both linear approximations are necessary.

Then the condition $|c| \ll 1$ leads to

$$|k_r| \ll 1$$

$$|k_e| \ll 1$$

Under the last two inequalities one can see that N becomes many times less than the equilibrium value N^{eq} much earlier than $\nu_a = \nu_{a0}$ and the transition is actually over. So, the point of decompositions has to shifted.

The shift of decompositions has to lead to the basic point situated at the position characteristic for the relatively intensive flow. One of the possible recipes is to choose the point ν_a^* of decomposition according to

$$N(\nu_a)W_a^+ = \int_0^{\nu_a^*} J d\nu_a'$$

The last condition can be approximately rewritten as

$$W_a^+ = \frac{1}{|k_r| + |k_e|} \frac{1 - J(\nu_a^*)}{N}$$

---

[9]Take a cross section $\{\nu_b = const\}$.

[10]Then the cross of the ridge can not disturb the equilibrium distribution. So, the flow is known.

One can start instead of $\nu_a = 0$ from infinity and get a similar estimate. Also it is reasonable to consider

$$W_a^+ = \frac{1}{|k_r| + |k_e|} \frac{J(\nu_a^*)}{2N}$$

as the point for decompositions.

Here naturally appears the length Δ of the region where the transition occurs. It can be estimated as

$$\Delta = \frac{1}{|k_r| + |k_e|}$$

So, the soft shift can be greater than this region.

We continue to consider the problems of the differential approach.

- Another problem is the smallness of $|k_e|$, $|k_r|$. Because of the monotonous character of derivatives of the free energy along channels and ridges it can be attained only near the saddle point. But here the square approximation has to be used and the Stauffer's solution will be the answer.

  Certainly, if the value of ν_a is extremely big one can observe small values of derivatives rather far from the saddle point. But, although even here the discrete approach is preferable as it will be shown later.

Now the simplified approximate method for continuous case will be presented. In equation

$$\frac{d^2 N}{dx^2} - k_e \frac{dN}{dx} = N \frac{\exp(F_r - F_e)}{\Delta \nu_e \Delta \nu_r} \frac{W_{bx}^+}{W_a^+}$$

one can put $k_e \frac{dN}{dx}$ to zero because of the smallness of $|k_e|$.

Also because of the smallness of $|k_e|$, $|k_r|$ one can put very approximately

$$\frac{\exp(F_r - F_e)}{\Delta \nu_e \Delta \nu_r} \frac{W_{bx}^+}{W_a^+}$$

to some constant (let it be I_0). Then

$$\frac{d^2 N}{dx^2} = N I_0$$

Solution of the last equation is evident

$$N = A\exp(-\sqrt{I_0}x) + B\exp(\sqrt{I_0}x)$$

The requirement $N \to 0$ at $x \to \infty$ leads to

$$N = A\exp(-\sqrt{I_0}x) \tag{50}$$

But this solution has a bad behavior at $x \to -\infty$. So, in this region one has to use another approach. At $x \to -\infty$ the flow is very small and N is approximately equal to the equilibrium value N_{eq}. Then

$$\frac{d^2N}{dx^2} - k_e \frac{dN}{dx} = N_{eq}\frac{\exp(F_r - F_e)}{\Delta\nu_e \Delta\nu_r}\frac{W_{bx}^+}{W_a^+}$$

Then approximately

$$N = N_{eq} - \int J dx$$

or

$$N = N_{eq} - \int N_{eq}\frac{\exp(-(|k_e| + |k_r|)x)}{\Delta\nu_r \Delta\nu_e}dx\frac{W_{bx}^+}{W_a^+}$$

With the evident approximation for the equilibrium value N_{eq}:

$$N_{eq} = N_*\exp(-|k_e|x)$$

with parameter $N_* = N_{eq}(x = 0)$ one can get

$$N = N_{eq} - N_*\int \frac{\exp(-|k_r|x)}{\Delta\nu_r \Delta\nu_e}dx\frac{W_{bx}^+}{W_a^+}$$

Since one can approximately take $\Delta\nu_r \Delta\nu_e$ as a constant value there are no problems with integration. So,

$$N = N_{eq} - N_*\frac{1 - \exp(-|k_r|x)}{|k_r|\Delta\nu_r \Delta\nu_e}\frac{W_{bx}^+}{W_a^+}$$

These two solutions (let it be N_1 and N_2) have to be stuck together at the point where

$$N_1 = N_2$$

Another method can be formulated if we notice that (50) is valid namely locally because it was derived with a supposition $I_0 = const$. So, we have to go to the local form by differentiation of (50) which gives

$$\frac{dN}{dx} = -NI_0$$

This equation can be integrated with arbitrary I_0 which leads to

$$N \sim \exp(-\int I_0(x')dx')$$

When the evident known functional form

$$I_0 \sim exp(cx)$$

is taken, one can come to

$$N \sim \exp(-\frac{I_{00}}{c}\exp(cx))$$

with parameter I_{00}. Certainly, parameters I_{00} and c can be considered here as the fitting parameters.

The functional form announced above resembles Θ-function with a soft transition from 1 to 0. We shall call it as a soft Θ-function and denote it by

$$S(x) = \exp(-\exp(x))$$

This function can be used as a brick in an ansatz

$$Q = \sum A_i S(a_i(x - x_i))$$

which can be very effectively used as an approximate solution in all situations considered below in this paper.

5 Interaction of valleys

5.1 Coordinates of valley in the ν_a, ν_b coordinate system

The coordinate of the valley is given by the condition

$$\frac{\partial F(\nu_a, \nu_b)}{\partial \nu_b} = 0$$

The straight differentiation of the free energy gives

$$\frac{\partial F}{\partial \nu_b} = \frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]$$

$$-b_b - [\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}]$$

where S is the surface square of the embryo. In simplest approximation it can be written as

$$S = (v_a\nu_a + v_b\nu_b)^{2/3}$$

The standard Gibbs-Duhem's equation looks like

$$\nu_a db_a + \nu_b db_b = 0$$

and leads to

$$[\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] = 0$$

This brings the condition for the valley coordinate to

$$\frac{\partial F}{\partial \nu_b} = \frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] - b_b$$

But due to the surface enrichment the concentration differs from

$$\xi = \frac{\nu_a}{\nu_a + \nu_b}$$

and has to be

$$\xi = \frac{\nu_a - S\varrho_a}{\nu_a - S\varrho_a + \nu_b - S\varrho_b}$$

Then the Giibs-Duhem's equation looks like

$$Sd\gamma + \nu_a db_a + \nu_b db_b = 0$$

and leads to

$$\frac{d\gamma}{d\xi}\frac{\partial \xi}{\partial \nu_b}S + [\frac{\partial b_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] = 0$$

and

$$\frac{\partial F}{\partial \nu_b} = \gamma\frac{2}{3}S^{-1/2}[v_b + \frac{\partial v_a}{\partial \xi}\nu_a\frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi}\nu_b\frac{\partial \xi}{\partial \nu_b}] - b_b$$

The careful analysis of the generalization of the Gibbs-Duhem's equation for the embryos shows that the terms

$$\frac{\partial v_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_b}$$

have to vanish together with

$$\frac{d\gamma}{d\xi} \frac{\partial \xi}{\partial \nu_b} S + [\frac{\partial b_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_b}]$$

Really, the Kelvin's relation in the saddle point requires that

$$\frac{b_a}{v_a} = \frac{b_b}{v_b} \tag{51}$$

The direct calculation with a non zero value of the last terms gives

$$\frac{b_b}{[v_b + \frac{\partial v_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_b}]} = \gamma(36\pi)^{1/2} \frac{2}{3} S^{-1/2} = \frac{b_a}{[v_a + \frac{\partial v_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_a} + \frac{\partial v_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_a}]}$$

and one can come to (51) only if these terms vanish.

Generally speaking the Gibbs-Duhem's equation has to written in the form

$$\sum (differentials \; of \; all \; intensive \; variables) * (corresponding \; intensive \; variables) = 0$$

Particularly

$$S d\gamma + \nu_a db_a + \nu_b db_b + \nu_a dv_a + \nu_b dv_b = 0$$

Then

$$\frac{d\gamma}{d\xi} \frac{\partial \xi}{\partial \nu_b} S + \gamma \frac{2}{3} S^{-1/2} [\frac{\partial v_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_b} + \frac{\partial v_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_b}] - [\frac{\partial b_a}{\partial \xi} \nu_a \frac{\partial \xi}{\partial \nu_b} + \frac{\partial b_b}{\partial \xi} \nu_b \frac{\partial \xi}{\partial \nu_b}] = 0$$

and

$$\frac{\partial F}{\partial \nu_b} = \gamma \frac{2}{3} S^{-1/2} v_b - b_b$$

One can see that the concentration of valley satisfies the condition

$$\gamma \frac{2}{3 b_b(\xi)} (v_a(\xi) + v_b(\xi^{-1} - 1))^{-1/3} = \nu_a^{1/3}$$

and it is not a constant value. Moreover, it is evident that valleys in the ν_a, ν_b system of coordinates do not coincide with channels in κ, ξ system of coordinates. They coincide only in saddle points. The valleys in ν_a, ν_b system can appear and disappear, their position in the absence of hierarchy of kinetic coefficients means nothing.

5.2 Asymptotics at $\nu_b \to \infty, \nu_a - fixed$

The necessary condition of applicability of solution of Trinkaus is the limit

$$\nu_b \to \infty, \ \nu_a = fixed \quad F \to -\infty$$

The explicit calculation gives

$$\nu_b \to \infty, \ \nu_a = fixed \quad F \to -b_b \zeta_b$$

So, it is necessary that $\zeta_b > 0$. But the last condition is not a necessary condition for nucleation in a gas mixture. The necessary condition is the existence of concentration ξ for which the function $b_a \xi + b_b (1 - \xi)$ is negative. So, there exists a situation when there is no behavior necessary for application of the Trinkaus' solution.

When $b_b > 0$ one can see the asymptotic wing with a negative slope. It will be called simply as "wing".

Otherwise there can be a situation when even with $b_b > 0$ nucleation can go from one valley to another (may be more deep) valley and further no transition to $\nu_b \to \infty$, $\nu_a = fixed$ will take place because of the height of a new (further) ridge.

In the case of purely supersaturated vapor of components the wings have to be included in the general picture of relief of the free energy.

5.3 Two valleys. Kinetic equation

The previous consideration shows that the most ordinary situation is the jump of embryo from one valley to the neighbor one. In one valley (let it be called as the "source valley" and marked by the subscript $-$) the embryos are in the pre-critical region (i.e. $\kappa < \kappa_c$) and in the other valley (let it be called as the "destination valley" and marked by the subscript $+$) the embryos are in the post-critical region (i.e. $\kappa > \kappa_c$). The transitions take place along lines $\nu_a = const$. Since the increase of ν_b leads to the increase of κ it is quite possible.

The values of ν_b at the ridge will be marked as ν_{br}. The values of ν_b at the bottom of the source valley will be marked as ν_{be-} and the values of ν_b at the bottom of the destination valley will be marked as ν_{be+}. All these values are taken in the ν_a, ν_b coordinate system.

Kinetic equations are rather transparent and look like

$$\frac{dN_-}{dt} = W_{as}^+(\nu_a - 1, \nu_{be-})N_-(\nu_a - 1) - W_{as}^+(\nu_a, \nu_{be-})N_-(\nu_a)$$

$$(52)$$

$$+W_{as}^-(\nu_a + 1, \nu_{be-})N_-(\nu_a + 1) - W_{as}^-(\nu_a, \nu_{be-})N_-(\nu_a) - J_-(\nu_a) + J_+(\nu_a)$$

$$\frac{dN_+}{dt} = W_{ad}^+(\nu_a - 1, \nu_{be+})N_+(\nu_a - 1) - W_{ad}^+(\nu_a, \nu_{be+})N_+(\nu_a)$$

$$(53)$$

$$+W_{ad}^-(\nu_a + 1, \nu_{be+})N_+(\nu_a + 1) - W_{ad}^-(\nu_a, \nu_{be+})N_+(\nu_a) - J_+(\nu_a) + J_-(\nu_a)$$

Here N_- and N_+ are the numbers of embryos with given ν_a in a valley (in ν_a, ν_b system of coordinates), W_+ and W_- are direct and inverse absorption coefficients, J_- is the flow from the source valley to the destination valley, J_- is the flow from the destination to the source valley (the inverse flow).

We shall investigate the stationary solution.

One has to take into account that W_a^+ and W_a^- are functions of ν_b. They are taken at ν_b equal to the values at the bottom of valley. This can be done because of the relative narrowness of valleys which goes from representation in κ, ξ variables.

5.4   Two valleys. Direct and inverse flows

The values of flows J_- and J_+ are given by the standard formulas

$$J_- = N_- \frac{\exp(-F_r + F_{e-})}{\Delta_r \nu_b \Delta_{e-} \nu_b} W_{bx}^+$$

$$J_+ = N_+ \frac{\exp(-F_r + F_{e+})}{\Delta_r \nu_b \Delta_{e+} \nu_b} W_{bx}^+$$

Here F_r is a free energy of the embryo at the ridge (in ν_a, ν_b coordinates), F_{e-} is the free energy of the bottom of the source valley in ν_a, ν_b coordinate system, F_{e+} is the free energy of the bottom of the destination valley in ν_a, ν_b coordinate system.

The value of $\Delta_r \nu_b$ is given by

$$\Delta_r \nu_b = \sum_{\nu_b = \nu_{br1}}^{\nu_{br2}} \exp(-F_r + F(\nu_a, \nu_b))$$

Here ν_{br1} and ν_{br2} are chosen as roots of equation

$$F(\nu_a, \nu_b) = (2F_r + F_{e+} + F_{e-})/4$$

closest to ν_{br} and

$$\nu_{br1} < \nu_{br} < \nu_{br2}$$

The value of $\Delta_{e-}\nu_b$ is given by

$$\Delta_{e-}\nu_b = \sum_{\nu_b=\nu_{be-1}}^{\nu_{be-2}} \exp(F_{e-} - F(\nu_a, \nu_b))$$

Here ν_{be-1} and ν_{be-2} are chosen as roots of equation

$$F(\nu_a, \nu_b) = (F_r + F_{e-})/2$$

closest to ν_{be-} and

$$\nu_{be-1} < \nu_{be-} < \nu_{be-2}$$

The value of $\Delta_{e+}\nu_b$ is given by

$$\Delta_{e+}\nu_b = \sum_{\nu_b=\nu_{be+1}}^{\nu_{be+2}} \exp(F_{e+} - F(\nu_a, \nu_b))$$

Here ν_{be+1} and ν_{be+2} are chosen as roots of equation

$$F(\nu_a, \nu_b) = (F_r + F_{e+})/2$$

closest to ν_{be-} and

$$\nu_{be+1} < \nu_{be+} < \nu_{be+2}$$

In continuous approximation one can get the following equations

$$\Delta_r \nu_b = \int_{\nu_b=\nu_{br1}}^{\nu_{br2}} \exp(-F_r + F(\nu_a, \nu_b)) d\nu_b$$

$$\Delta_{e-}\nu_b = \int_{\nu_b=\nu_{be-1}}^{\nu_{be-2}} \exp(F_{e-} - F(\nu_a, \nu_b)) d\nu_b$$

$$\Delta_{e+}\nu_b = \int_{\nu_b=\nu_{be+1}}^{\nu_{be+2}} \exp(F_{e+} - F(\nu_a, \nu_b)) d\nu_b$$

One can prove that in frames of inequalities lying in the base of capillary approximation the continuous approximation is valid. One can also prove

that in the absence of peculiarities in behavior of the free energy it is possible in the capillary approximation to use the square approximation with infinite limits for calculation of the mentioned values. This gives

$$\Delta_r \nu_b = \sqrt{\pi} \left(-\frac{1}{2} \frac{\partial^2 F(\nu_a, \nu_b)}{\partial \nu_b^2} \Big|_{\nu_b = \nu_{br}} \right)^{-1/2}$$

$$\Delta_{e-} \nu_b = \sqrt{\pi} \left(\frac{1}{2} \frac{\partial^2 F(\nu_a, \nu_b)}{\partial \nu_b^2} \Big|_{\nu_b = \nu_{be-}} \right)^{-1/2}$$

$$\Delta_{e+} \nu_b = \sqrt{\pi} \left(\frac{1}{2} \frac{\partial^2 F(\nu_a, \nu_b)}{\partial \nu_b^2} \Big|_{\nu_b = \nu_{be+}} \right)^{-1/2}$$

One can rewrite equations for J_- and J_+ as following

$$J_- = N_- I_-$$

$$J_+ = N_+ I_+$$

where I_+ and I_- are independent on N_+, N_-.

Already now one can fulfill the qualitative analysis of the kinetic equations.

5.5 Qualitative analysis of the kinetic equations

Consider the region of ν_a where $W_a^+(\nu_a, \nu_{be-}) \sim I_-$. It is easy to see that at ν_a corresponding to the possible transition from one valley to another

$$W_a^+(\nu_a, \nu_{be-}) < W_a^-(\nu_a, \nu_{be-})$$

(otherwise the saddle point in the source valley is already over)

$$W_a^+(\nu_a, \nu_{be+}) > W_a^-(\nu_a, \nu_{be+})$$

(otherwise it will be necessary to overcome the saddle point in the destination valley and it will cause the establishing of the equilibrium distribution until the height of the saddle point; moreover there is a straight way without barriers to the origin of coordinates).

It means that

$$F(\nu_a, \nu_{be-}) < F(\nu_a + 1, \nu_{be-})$$
$$F(\nu_a, \nu_{be+}) > F(\nu_a + 1, \nu_{be+})$$

Moreover one can see that

$$F(\nu_a, \nu_{br}) > F(\nu_a + 1, \nu_{br})$$

(otherwise it is more profitable to overcome the ridge earlier at smaller ν_a).

Practically in the main order

$$\frac{I_-}{I_+} = \exp(+F_{e-} - F_{e+})$$

The ratio I_-/I_+ governs the evolution of the process. One can see two characteristic situations here

- Situation
$$I_- \gg I_+$$

  Here one can see that the solution of the previous section can be directly applied. The destination valley do not affect the distribution in the source valley. So, one can put $J_+ = 0$ and split the system of equations. Only the first equation is essential and solution is really the solution in the situation discussed above.

- Situation
$$I_- \ll I_+$$

  This situation has no analogs and has to be considered separately.

5.6 Situation

$$I_- \ll I_+$$

One can approximately put

$$W_a^+(\nu_a, \nu_{be-}) \simeq W_a^+(\nu_a, \nu_{be+})$$

This is taken only for simplicity.

Approximately, the condition of the beginning of the jump of embryos, which changes N_- is the following

$$I_- \geq W_a^+(\nu_a, \nu_{be-})$$

Then
$$I_+ \gg W_a^+(\nu_a, \nu_{be-})$$

Then the second equation of the system becomes the following

$$J_- = J_+$$

and we have locally in a rough approximation

$$\frac{dN_-}{dt} = W_a^+(\nu_a - 1, \nu_{be-})N_-(\nu_a - 1) - W_a^+(\nu_a, \nu_{be-})N_-(\nu_a)$$
$$\tag{54}$$
$$+W_a^-(\nu_a + 1, \nu_{be-})N_-(\nu_a + 1) - W_a^-(\nu_a, \nu_{be-})N_-(\nu_a)$$

Then

$$\frac{N_-}{\Delta_{e+}\nu_b} = \frac{N_+}{\Delta_{e-}\nu_b} \exp(-F_{e-} + F_{e+})$$

and approximately

$$\frac{N_+}{N_-} = \exp(F_{e-} - F_{e+})$$

The point where

$$I_- \approx W_a^+(\nu_a, \nu_{be-})$$

will be marked as $\nu_a = y_0$. When ν_a increases one has

$$I_- \gg W_a^+(\nu_a, \nu_{be-})$$

$$I_+ \gg W_a^+(\nu_a, \nu_{be-})$$

This ensures the quasi-equilibrium and actually the common valley. Later one attains y_1 where

$$F_{e-}(y_1) = F_{e+}(y_1)$$

For $\nu_a > y_1$ one has

$$I_- \gg I_+$$
$$J_- = J_+$$
$$N_+ \gg N_-$$

It will be until y_2 defined by condition

$$I_+(y_2) = W_a^+(\nu_a = y_2, \nu_{be-})$$

(also the soft shift has to be added). Later all remaining embryos from the source valley go into the destination valley. But their total quantity is already rather small. So, we need not to consider this process in details.

The main conclusion results in the appearance of the common valley with a new free energy F_0. Here there is no connection with the absence of excesses. This free energy can not be defined separately from the width of the equilibrium distribution, only the ratio

$$\exp(-F_0)/\Delta_{e0}\nu_b$$

can be determined. But namely this ratio is the equilibrium distribution and in the expression for the nucleation rate.

The last ratio can be determined from

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e-})}{\Delta_{e-}\nu_b} + \frac{\exp(-F_{e+})}{\Delta_{e+}\nu_b}$$

Very approximately one can say that

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e-})}{\Delta_{e-}\nu_b}$$

when $F_{e-} < F_{e+}$ and

$$\frac{\exp(-F_0)}{\Delta_{e0}\nu_b} = \frac{\exp(-F_{e+})}{\Delta_{e+}\nu_b}$$

when $F_{e-} > F_{e+}$.

5.7   Intermediate situation

• Intermediate situation is very rare because it can take place only under the simultaneous realization of two equations

$$I_- = I_+$$

and

$$I_- = W_a^+(\nu_a, \nu_{be})$$

(also the soft shift has to taken into account). But this case in the only one where the interaction of valleys and the exhaustion of the equilibrium distribution play simultaneously.

Solution of this situation is rather simple - it is necessary to solve the system of several algebraic equations. At small

$$\nu_b < y_0$$

where

$$W_a^+(\nu_a, \nu_{be-}) \gg I_-$$

one has to use the boundary condition

$$N_- = N_{-eq} \sim \exp(-F(\nu_a, \nu_{be-})/\Delta_{e-}\nu_b$$

$$N_+ \ll N_{+eq} \sim \exp(-F(\nu_a, \nu_{be+})/\Delta_{e+}\nu_b$$

At big

$$\nu_b > y_0$$

where

$$W_a^+(\nu_a, \nu_{be-}) \ll I_-$$

one has to use another boundary condition

$$N_- \ll N_{-eq}$$

$$I_+ = 0$$

if it will be necessary. So, the task is to solve several simple algebraic equations. Certainly, the discrete approach is preferable in the computation.

To come to the continuous approximation one has to change the finite differences for derivatives which approximately leads to the following kinetic equations

$$\frac{\partial N_-}{\partial t} = W_a^+(\nu_a, \nu_{be-})[k_{e-}\frac{\partial N_-}{\partial \nu_a} + \frac{\partial^2 N_-}{\partial \nu_a^2}] - J_-(\nu_a) + J_+(\nu_a)$$

$$\frac{\partial N_+}{\partial t} = W_a^+(\nu_a, \nu_{be+})[\frac{\partial^2 N_+}{\partial \nu_a^2} + k_{e+}\frac{\partial N_+}{\partial \nu_a}] - J_+(\nu_a) + J_-(\nu_a)$$

Here

$$k_{e-} = -(1 - \exp(\partial F(\nu_a \nu_{be-})/\partial \nu_a)) \approx \partial F(\nu_a \nu_{be-})/\partial \nu_a$$

$$k_{e+} = 1 - \exp(\partial F(\nu_a \nu_{be+})/\partial \nu_a) \approx -\partial F(\nu_a \nu_{be+})/\partial \nu_a$$

Continuous approximation can not be widely spread but can be applied only in rather specific situations. The reasons are similar to those described in analysis of the Trinkaus' solution. The proximity of $dF_r/d\nu_b$ and both $dF_{e+}/d\nu_b$ and $dF_{e-}/d\nu_b$ to zero means the proximity to the saddle point where the linear approximation fails.

The simple approximate method is the iteration one - the values J_- and J_+ are calculated on the base of previous approximations and they are treated as known functions. Initial approximations are following:

- when the source valley are deeper than the destination one, then there is the quasi-equilibrium.

- when the destination valley are deeper than the source one, then there is the Trinkaus' solution or the corresponding simplified solution.

This method is very effective and leads to a rather precise solution after one or two iterative steps.

It is necessary to stress here the effectiveness of the method based on the ansatz with the soft Heavisaid's functions.

The main result of this section which was the goal of the whole publication is the radical change of the nucleation rate. The main goal is achieved - the change of the nucleation rate in the orders of magnitudes is shown. One can also see that the rate of nucleation does not depend on the free energy in saddle point but on the mutual position of valleys and ridges and their relative heights. Certainly, the problem to find the nucleation rate includes now the determination of many characteristics and is more complex than in the theories suggesting the recipes based on the value of the free energy in one point. The theory presented here has to be used in order to get the true value of the free energy. Now the problem is transformed in the thermodynamic area - it is necessary to find the free energy of the embryo formed in the mixture of vapors. This problem is complex enough to continue investigations of the binary and multicomponent nucleation.

6 Paths of transition

Now one can return to the general situation to see how the real transition from the pre-critical region to the post-critical region will occur.

The problem is to see where the real change of the channels will take place. This problem will be solved here. So, here the analysis will be mainly qualitative. All details of transition between channels will be a subject of a separate analysis.

6.1 Approximate position of the valley

To get the approximate position of valley and the ridge one can act without surface excesses.

Consider the channel in coordinates ν_a, ξ. Then

$$\nu_a = \kappa/p(\xi)$$

where $p(\xi)$ is a known function and

$$F = -B(\xi)p(\xi)\nu_a + p^{2/3}(\xi)\nu_a^{2/3}$$

The coordinate of the valley is given by condition

$$\frac{\partial F}{\partial \xi} = 0$$

or

$$-B'(\xi)p(\xi)\nu_a - B(\xi)p'(\xi)\nu_a + \frac{2}{3}p^{2/3}(\xi)\nu_a^{-1/3}p'(\xi) = 0$$

At the saddle point

$$-B(\xi)p'(\xi)\nu_a + \frac{2}{3}p^{2/3}(\xi)\nu_a^{-1/3}p'(\xi) = 0$$

and the saddle point of valley coincides with the saddle point of the channel line, since

$$B'(\xi) = 0$$

Asymptotically at $\nu_a \to \infty$ one can get

$$-B'(\xi)p(\xi) - B(\xi)p'(\xi) = 0$$

One can see that the function p is rather smooth while B is rather sharp. This condition is a definition of a "clear channel". Then one can neglect $B(\xi)p'(\xi)$ in comparison with $B'(\xi)p(\xi)$. This leads to

$$-B'(\xi)p(\xi) = 0$$

and because of $p \neq 0$ the last equation coincides with the coordinate of the channel. So, we see that the valley is near the channel line for every ν_a.

To see the behavior at moderate ν_a near the critical values one can note that p' attains a moderate value. Really

$$p' = \frac{\partial^2 \kappa}{\partial \nu_a^2} \sim 1$$

(we choose the space scale to have the volume for a molecule in a liquid phase the order of 1). Then one has to take into account that

$$\kappa_c = 2/(3 max\ B(\xi)) \gg 1$$

requires $max\ B \ll 1$ Then the term $B(\xi)p'(\xi)\nu_a$ has a small parameter. The term $p^{-1/3}(\xi)\nu_a^{-1/3}p'(\xi)$ has the same order as $B(\xi)p'(\xi)\nu_a$ and, thus, is small. This reduces the coordinate of a value to coordinate of a channel.

The same analysis can be done for every ridge. The general approximate conclusion is that every separation line corresponds to the ridge and their coordinates are similar.

At $\nu_a \to 0$ and $\kappa \to 0$ the leading term is

$$\frac{2}{3}p^{2/3}\nu_a^{2/3}p'$$

which means that the valley does not exist. So, the valley can not directly start at $\nu_a = 0$ in continuous approximation. Fortunately, ordinary this effect takes place at ν_a less than 1.

All above considerations are very approximate and they are used only to see that qualitatively nothing is changes when we consider valleys instead of channels.

Approximately speaking every channel corresponds to one valley, their coordinates are rather similar.

Precisely speaking one can see many specific peculiarities, for example, the appearance of valleys without corresponding channels. But the probability of such peculiarities is very low. As a rule these valleys are not deep enough and can be treated as negligible ones.

71

6.2 Transition zones

Consider the pair of valleys.

Every valley (index v) can be considered as a source valley (s). Every valley can be considered as a destination valley (d). One can imagine many pairs of source and destination valleys. Every pair has to be investigated.

At first we consider the situation when the channels are neighbor ones. The ridge is the maximum of F at the band $\nu_a = const$ between the concentration ξ_s of a source valley and the concentration ξ_d of a destination valley.

We define F_v as the free energy at the valley, F_r the free energy at the ridge.

Now we shall make use from the approximate functional form for F_r, F_v established above

$$F = const_1 \nu_a^{2/3} - const_2 \nu_a$$

One can see the following facts

- Every valley has only one critical ν_{avc} point determined by

$$dF_v/d\nu_a = 0$$

- One can define the pre-critical region of the valley where $dF_v/d\nu_a > 0$ and post-critical region of valley where $dF_v/d\nu_a < 0$. There is only one pre-critical region with a size $\nu_a < \nu_{avc}$ and a post-critical region where $\nu_a > \nu_{avc}$.

- Every ridge has only one critical ν_{avc} point determined by

$$dF_r/d\nu_a = 0$$

- One can define the pre-critical region where $dF_r/d\nu_a > 0$ and post-critical region of ridge where $dF_r/d\nu_a < 0$. There is only one pre-critical region with a size $\nu_a < \nu_{arc}$ and a post-critical region where $\nu_a > \nu_{arc}$.

The real effect on the nucleation rate occurs when there is a transition from the pre-critical part of the source valley to the post-critical part of a destination valley. Transition from the post-critical part is useless because the embryos can simply continue to grow, they already overcame the barrier. So, there is no need to overcome another one barrier and this case is out of our interest.

At first we suppose that in the whole pre-critical part of the destination channel there is an equilibrium distribution. It means that there is no further change of channels and the destination channel will be the final destination channel. So, there is only one cascade - only one change of the channel. We shall call such processes as one-cascade processes.

One can choose components in such a way that the first component is a rapid one.

Consider the regions where the probability to change the channel is greater than to increase the value of slow components in the old channel. This corresponds to condition

$$W_{sl} \leq W_1 Z_1 \exp(F_r - F_s)$$

Here the kinetic coefficient W_{sl} is the total kinetic coefficient of all slow components, W_1 is the kinetic coefficient of a rapid component and Z_1 is the corresponding Zel'dovich factor for transition over the ridge. The last inequality can be expressed in terms of the $F_r - F_v$ as

$$F_r - F_v \leq \ln(W_{sl}/(W_1 Z_1)) \equiv \Delta_t$$

The rhs is a very slowly varying function. Approximately it is a constant.

Consider

$$\Delta = F_r - F_v$$

According to the approximate formulas the function $\Delta(\nu_a)$ has the second derivative

$$\frac{d^2\Delta}{d\nu_a^2} = -[p^{2/3}(\xi_r) - p^{2/3}(\xi_v)]\frac{2}{9}\nu_a^{-4/3}$$

which has a constant sign.

Thus, Δ has no more than maximum (it will be marked by the index "m").

Certainly, the condition $F_r - F_v = \Delta_t$ depends on the scale of ν_a. It is necessary to choose the scale of ν_a-axis to have

$$d\Delta/d\nu_a \sim 1$$

at $\Delta \simeq \Delta_t$. Since Δ is not a too sharp function of ν_a, it is easy to do. The condition $\Delta < \Delta_t$ can be valid no more than in two zones: one before ν_{am} another later ν_{am}. Namely, in intervals

$$[0, \nu_{at-}], \quad [\nu_{at+}, +\infty]$$

the last condition is valid.

One can make the following notes:

- The second interval $[\nu_{at+}, +\infty]$ can be absent when

$$B(\xi_r)p(\xi_r) < B(\xi_s)p(\xi_s)$$

- The first interval also can be effectively (not precise) absent when $\nu_{at-} < 1$ which occurs rather often.

- One can come to the situation when valleys are purely isolated.

- One has to keep in mind that the approximate formulas take place only at big ν_a.

The interval $[0, \nu_{at-}]$ will be called as the "pre-transition zone", the interval $[\nu_{at+}, +\infty]$ - as the "post-transition" zone.

Consider the question about the mutual position of the destination and the source channels. The definition of κ as even without microscopic corrections $(\sum \nu_i v_i)\gamma^{3/2}$ contains γ and v_i and is a very complex function. But in the majority of situations the increase of ν_a (other ν_i are fixed) causes the increase of κ. We shall imply this property to take place. This property will be referred as the property of κ-convexity. The line $\kappa = const$ as a function of ν_a is convex.

Certainly, in real systems there can be concave regions, where the growth of ν_a leads to the change of concentration, the partial volumes change, the surface tension change and the value of κ falls. But this situation is exclusive.

Under the property of convexity one can see that the transition will be carried out only by addition of molecules of the first component (ejection is not possible) and will go from the left side to the right side in ν_a, ν_b plane.

The precise position of boundaries have to be defined with surface excesses. Also a shift connected with a special renormalization has to be taken into account.

6.3   Nucleation conditions and supplying conditions

Here we shall mark ν_a by x.

Conditions for the possibility of nucleation through the post-transition zone are the following ones

- Transition has to be effective, i.e. there has to be a region in the post-critical region in a destination valley $x > x_{dc}$ where $F_d(x) < F_{sc}$ Certainly this region looks like

$$[x_b, +\infty]$$

and the beginning of this region has to be smaller than x_{sc}:

$$x_b < x_{sc}$$

- Transition has to be opened, i.e.

$$x_{t+} < x_{sc}$$

The beginning of transition will be at

$$x_w = max\{x_b, x_{t+}\}$$

There are two possibilities at x_w:

- The first possibility
$$F_d(x_w) > F_s(x_w)$$

Here the common valley will be formed and the most effective transition will be at x_u defined as

$$F_d(x_u) = F_s(x_u)$$

- The second possibility

$$F_d(x_w) < F_s(x_w)$$

Here the transition from valley to valley occurs like a falling from the high channel to the low channel. Solution looks like the Trinkaus' one.

To see the real process of the channel transition it is necessary to have corresponding conditions at the beginning of transition. These conditions have to be the equilibrium conditions. It is necessary that earlier in the valley there would be no possibility to escape from the valley. One has to analyze such possibility.

To see the transition in the pre-transition zone it is necessary that two conditions take place

- The first condition:
$$F_d(x) < F_s(x_w)$$

- The second condition:

  Transition has to lead to the post-critical region in the destination valley.

We are interested to avoid such intensive transition which can destroy the equilibrium conditions at x_w.

Since F_d has to be at the post-critical region, it is a decreasing function of x and it is sufficient to check condition at the boundary:

$$F_d(x_{t-}) < F_s(x_w)$$

In this situation the intensity of the valley transition in the pre-transition zone is so big that there is no equilibrium condition for the transition in the post-transition zone.

Since the transition in the pre-transition zone has to lead to the post-critical zone then the peak of F_d lies inside the transition through the pre-transition zone. So, since

$$maxF_d > maxF_s > F_s(x_w)$$

the transition occurs in a manner of common channel and the real transition takes place at x_p when
$$F_d(x_p) = F_s(x_p)$$

if
$$x_p < x_{t-}$$

If at
$$x = x_{t-}$$

we have
$$F_d > F_s$$

the most intensive transition takes place at x_{t-}. This situation is more probable than the precedent one.

What has to be done when the condition

$$F_d(x_{t-}) > F_s(x_{t-})$$

takes place?

Certainly, the transition can take place out of pre-transition and post-transition zones but with a very low probability. To take into account this possibility one has to add to F_s the quantity $F_r - F_s - \Delta_t$, i.e. to go from F_s to $F_r - \Delta_t$. This has to be done out of pre- and post-transition zones.

The point of transition will be near the root of equation

$$F_d = F_r - \Delta_t$$

Let it be at $x = x_y$.

This transition can not violate the equilibrium. So, the transition in the post-transition zone is not destroyed and intensities of this transition and transition in the post-transition zone have to be compared (added).

We shall call this transition as "the saturation transition".

Here the transition is going across the ridge into the valley. The surface excesses can be taken into account very simply by noticing that the forms of ridge and valley profiles remain the old ones and only the shifts of profiles as a whole take place due to the account of excesses.

6.4   Details of the saturation transition

Solution of the saturation transition is rather simple. Consider at first the general situation. Let $n_d(\nu_a)$ be the embryos number density in a destination valley, $n_s(\nu_a)$ be the embryos number density in a source valley, The evolution equation for the source valley looks like

$$\frac{\partial n_s}{\partial t} = -\frac{\partial}{\partial \nu_a} W_{as}^+ n_s^e(\nu_a) [\frac{n_s(\nu_a)}{n_s^e(\nu_a)} - \frac{n_s(\nu_a + 1)}{n_s^e(\nu_a + 1)}] -$$

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W_{bx}^+ + n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W_{bx}^+$$

Here W_a is kinetic coefficient, n^e is the equilibrium distribution, the flow

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s) W_{bx}^+$$

is the flow from the source valley to the destination valley and

$$n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d) W_{bx}^+$$

is the flow from the destination valley to the source valley. The value Z is the Zeldovich' factor, Δ is the normalizing factor.

Analogously one can write equation for the destination valley

$$\frac{\partial n_d}{\partial t} = -\frac{\partial}{\partial \nu_a} W_{ad}^+ n_d^e(\nu_a)[\frac{n_d(\nu_a)}{n_d^e(\nu_a)} - \frac{n_d(\nu_a+1)}{n_d^e(\nu_a+1)}]+$$

$$n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s)W_{bx}^+ - n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d)W_{bx}^+$$

In continuous approximation

$$\frac{\partial n_s}{\partial t} = W_{as}^+[\frac{\partial^2}{\partial \nu_a^2} n_s(\nu_a) + \frac{\partial F_s}{\partial \nu_a}\frac{\partial}{\partial \nu_a} n_s(\nu_a)]$$

$$(55)$$

$$-n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s)W_{bx}^+ + n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d)W_{bx}^+$$

for the source valley and

$$\frac{\partial n_d}{\partial t} = W_{ad}^+[\frac{\partial^2}{\partial \nu_a^2} n_d(\nu_a) + \frac{\partial F_d}{\partial \nu_a}\frac{\partial}{\partial \nu_a} n_d(\nu_a)] -$$

$$(56)$$

$$n_d \frac{Z_d}{\Delta_d} \exp(-F_r + F_d)W_{bx}^+ + n_s \frac{Z_s}{\Delta_s} \exp(-F_r + F_s)W_{bx}^+$$

for the destination valley.

One can assume that

$$\frac{\partial F_d}{\partial \nu_a} = v_d \qquad \frac{\partial F_s}{\partial \nu_a} = v_s$$

are constants. Also it can be assumed that the linear approximations

$$- F_r + F_d = A_d x + \tilde{C}_d \tag{57}$$

$$- F_r + F_s = A_s x + \tilde{C}_s \tag{58}$$

for $x = \nu_a - \nu_{a0}$ are valid. Here ν_{a0} is some parameter chosen as to belong to effective region of transition.

Then the stationary solutions will satisfy the system of equations

$$\frac{\partial^2}{\partial x^2} n_s + v_s \frac{\partial}{\partial x} n_s - C_s n_s \exp(A_s x) + C_d n_d \exp(A_d x) = 0 \tag{59}$$

78

$$\frac{\partial^2}{\partial x^2}n_d + v_d\frac{\partial}{\partial x}n_d - C_d n_d \exp(A_d x) + C_s n_s \exp(A_s x) = 0 \qquad (60)$$

with

$$C_s = \exp(\tilde{C}_s)Z_s W_{bx}^+/\Delta_s W_{as}$$

$$C_d = \exp(\tilde{C}_d)Z_d W_{bx}^+/\Delta_d W_{ad}$$

In the second solution because the region in the destination valley is the super-critical one it is possible to neglect $\frac{\partial^2}{\partial x^2}n_d$. Then the second equation is the linear first order differential equation with a known solution. Then after the substitution the first equation becomes the closed the closed equation. Since solution of (60) contains the integral then to get the differential equation it will be necessary to differentiate (59) one time and the resulting differential equation will have the order 3. It can not be solved at least in elementary functions. So, it is necessary to consider simplification based on classification of transitions.

These are three types of transitions - the non-equilibrium falling transition (first type), the equilibrium common valley transition (second type), the equilibrium saturation transition (third type). For different types we shall use different approximations.

For the first type it is possible to neglect

$$C_d n_d \exp(A_d x)$$

in the first equation. Then it becomes the closed equation

$$\frac{\partial^2}{\partial x^2}n_s - v_s\frac{\partial}{\partial x}n_s - C_s n_s \exp(A_s x) = 0 \qquad (61)$$

Then there is no necessity in validity of the linearization (58).

Solution of the last equation is presented above via cylindrical function.

The second equation is not necessary, but to complete the picture one can write it in the form

$$v_d\frac{\partial}{\partial x}n_d + C_s n_s \exp(A_s x) = 0 \qquad (62)$$

with the solution

$$n_d = -\int_{-\infty}^{x} C_s n_s \exp(A_s x')/v_d dx'$$

79

Certainly, the presentation of the solution via the cylindrical function is not convenient. It is more convenient to fulfill a block transformation and then to solve the system of several algebraic equations. We shall formulate this procedure. Really, one can go from x to kx to have

$$A_s k \approx \ln \alpha$$

where the parameter $\alpha \approx 1.5$. Then with an increase of x by 1 the intensity of transition increases 1.5 times. Then the equation (61) will be

$$k^{-2}\frac{\partial^2}{\partial x^2}n_s + v_s k^{-1}\frac{\partial}{\partial x}n_s - C_s n_s \alpha^x = 0 \tag{63}$$

Now it is possible to consider the interval $-2 < x < 2$ and to come back to the initial discrete form of equation

$$k^{-2}[n_s(x+1)-2n_s(x)+n_s(x-1)]+v_s k^{-1}[n_s(x+1)-n_s(x-1)]/2-C_s n_s(x)\alpha^x = 0 \tag{64}$$

These coupled algebraic equations have to be written at $x = -2, -1, 0, 1, 2$. At $x < -2$ one has to put n_s to the equilibrium value. So, there is a system of five coupled equations which can be easily solved.

One can continue analysis. Every band has a separate physical meaning:

- The band $x = 2$ is the starting band.

- At $x = -1$ one can use the smallness of the flow $C_s n_s(x)\alpha^x$ and the smallness of the deviation of n_s from the equilibrium value.

- The point $x = 0$ is the point where $|d/dx[(n_s - n_s^e)/n_s^e]|$ attains maximum and, thus,
$$d^2/dx^2[(n_s - n_s^e)/n_s^e] = 0$$

- At $x = 1$ one can assume that n_s is already small in comparison with n_s^e

- The values at $x = 2$ are the final values.

One can use these features at the characteristic zones to get analytic solutions and then the common solution will be their combination.

These approximations allow to solve this equation analytically by combination of the corresponding analytical band solutions. But the resulting

formulas will be very long to use them for calculations. To get concrete results it is more profitable to solve algebraic equations, the precision is rather high while the error is less than one tenth.

Certainly, one can directly solve the initial form of evolution equation described earlier as the discrete model.

The analysis of the first type is completed.

For the transition of the second type it is possible to neglect

$$\frac{\partial^2}{\partial x^2} n_s + v_s \frac{\partial}{\partial x} n_s$$

and

$$\frac{\partial^2}{\partial x^2} n_d - v_d \frac{\partial}{\partial x} n_d$$

Then both equations will be reduced to

$$- C_s n_s \exp(A_s x) + C_d n_d \exp(A_d x) = 0 \tag{65}$$

with the evident equilibrium solution as it was described earlier. The point $x = 0$ is the saddle point, i.e. the point where approximately $F_s = F_d$.

The third type of transition can be described in a following manner:

- Equation (59) leads to the fact that $n_s = n_s^e$. For n_s^e one can take approximation
$$n_s^e(x) = n_s^e(0) \exp(B_s x)$$

  where
$$B_s = -\frac{dF_s}{dx}\Big|_{x=0}$$

- Equation (60) looks like

$$v_d \frac{\partial}{\partial x} n_d - C_d n_d \exp(A_d x) + C_s n_s^e \exp(A_s x) = 0 \tag{66}$$

  and can be easily solved since it is the first order linear equation. The integral can be taken and the result will be expressed via Whittaker or Kummer functions which can be reduced to the Hypergeometric function.

81

The point $x = 0$ has to be chosen as $\arg(max\frac{dn_d}{dx})$.

Since the result can be expressed only in the form of special functions it is worth solving the discrete model. The method is quite the same and one can come to

$$k^{-2}\frac{\partial^2}{\partial x^2}n_d + k^{-1}v_d\frac{\partial}{\partial x}n_d - C_d n_d \exp(A_d kx) + C_s n_s(0)\exp((B_s + A_s)kx) = 0$$
(67)

The value of k has to be chosen to satisfy

$$k\min(A_d, A_s + B_s) = \alpha$$

Then algebraic equations will be

$$k^{-2}[n_d(x+1) - 2n_d(x) + n_d(x-1)] + k^{-1}v_d[n_d(x_1) - n_d(x-1)]/2$$
(68)
$$-C_d n_d \exp(A_d kx) + C_s n_s(0)\exp((B_s + A_s)kx) = 0$$

and have to be written at $x = -2, -1, 0, 1, 2$

Also it is necessary to mention the possibility to solve the discrete model from the very beginning. The starting equation will be

$$W_{ad}[n_d(x-1) - \frac{n_d^e(x-1)}{n_d^e(x)}n_d(x) - n_d(x) + \frac{n_d^e(x)}{n_d^e(x+1)}n_d(x+1)]$$
(69)
$$-C_d n_d \exp(A_d x) + C_s n_s^e \exp(A_s x) = 0$$

These equations are coupled algebraic equations. The initial condition is $n_d = 0$ at $x \to -\infty$.

Our consideration has to be completed by equation on parameters of transition.

The points of approximations $x = 0$ form the equations on parameters of the process. The possible presence of the special functions can be eliminated by rational approximations for special functions. Then the parameters of th process will be determined by the root of the algebraic equation.

Now one can see the general picture of transition. One can note that the complexity of the phase transition already between two valleys is rather essential. There are at least several possibilities to observe this transition

- Equilibrium transition in the pre-transition zone

- Equilibrium transition out of transition zone

- Equilibrium transition in the post-transition zone

- Falling transition in the post-transition zone

So, the unique approach to get the rate of nucleation is impossible.

One has to stress that already the equilibrium transitions can lead to the absence of equilibrium in valley with bigger x, and κ. This effect has to be taken into account to diminish the intensity of transition in the post-transition zone.

Here it becomes clear that the flow can split and merge. Beside these effects one can see the rapid change of the leading manner of the supercritical embryo formation. This is caused only by kinetic coefficients and, thus, it is reasonable to speak about "the kinetic rupture in the rate of nucleation".

One has to stress that in the saturation transition there is no difference whether the transition occurs in the open or in the forbidden zone. Really, $F_r - F_s$ can be greater than Δ_t:

$$F_r - F_s > \Delta_t$$

and the transition will take place. The only conditions is

-
$$F_r(\nu_a) - \Delta_t < F_{mc}$$

  where F_{mc} is the value at the saddle point with a minimal height and

-
$$F_d(\nu_a) < F_{sc}$$

  for some $\nu_a > \nu_{acd}$

Rigorously speaking the same consideration can take place for transition of other types.

Then one can come to the situation when both the equilibrium common channel transition and the falling transition can take place. When at some $\nu_a > \nu_{acd}$

$$F_d(\nu_a) = F_s(\nu_a) < F_{mc}$$

we have to examine F_r.

If
$$F_r - \Delta_t < F_{mc}$$
we see that the intensity of the common channel transition is greater than the intensity of transition through the saddle point.

Since F_d for $\nu_a > \nu_{acd}$ is a decreasing function this intensity is also greater than the intensity of a saturation transition. Then we have to compare it with the intensity of a falling transition.

If
$$F_r - \Delta_t < F_s$$
we have the common valley transition with intensity greater than the further falling transition.

If
$$F_r - \Delta_t > F_s$$
then the further falling transition will occur with intensity greater than the intensity of the common valley transition.

All this is done without account of the soft shift. To take this shift into account in a rough approximation it is necessary to add to Δ_t the quantity

$$\ln[\frac{d(F_r - F_s)}{d\nu_a}]^{-1}$$

6.5   Other peculiarities of transition

The property of the κ-convexity is very important in the context of the current analysis because it forbids the possibility to reach the pre-critical region after the transition through the post-transition zone. Otherwise there would be a source of embryos in some region of the destination valley. The property of the κ-convexity forbid the localization of the flow.

Such a localization of the transition flow can be seen in a multi-valley transition. Consider the situation when there is an intermediate valley (index i) and, thus, there are two ridges - one between the source valley and the intermediate valley (index rs), another between the intermediate valley and the destination valley (index rd). Suppose that for intermediate valley

$$F_{rs} - F_i < \Delta_t$$

$$F_{rd} - F_i < \Delta_t$$

Then one can speak about one effective ridge with a height

$$F_{rr} = max(F_{rs}, F_{rd})$$

Then the property of the ridge convexity disappears and the localization of the transition flow can be seen. One can speak about the

- Injection at the finite zone into the valley.

Earlier we consider only two components in the mixture. So, the inverse transition has to be the backward one. But in the three component mixture one can imagine the curved transitions - at first transition the concentration of the first component increases, at the second transition the concentration of the second component increases. However, it is necessary to have at least two rapid components in the mixture. In some special cases it is possible to return to the same valley but in another place of this valley - may be it is possible to jump from the pre-critical zone to the post-critical one, may be it is possible to make one loop of a spiral. Here the picture will be very picturesque. However, it would be very nice to see the concrete examples of such nucleating systems.

Here we do not consider the transitions from the post-critical zone of one valley to the post-critical zone of the other valley because this transition can not change the rate of nucleation.

Despite the transition will have now a very complex form the elementary bricks remain the same:

- the equilibrium common-valley transition

- the equilibrium saturation transition

- the non-equilibrium falling transition

The possibility to reach the rather transparent classification is based on the following simple approximate structure of every channel/separation line/valley/ridge:

- Every channel/separation line/valley/ridge has a pre-critical zone which is directly (without hills) connected with the origin, post-critical region with the irreversible growth (until infinity) and a small near-critical growth.

The last property takes place for every channel, separation line, valley and ridge.

According to the last analysis the multi-cascade transitions are not effective. Really, the cascade can lead to the post-critical region or to the pre-critical region. When it leads to the post-critical region it will be the last cascade. If it leads to the pre-critical region there is a smooth increasing path along the valley and this path will have at least the same intensity. So, the transition across the ridge is not effective here. As the result we see that there is only one main cascade in the multi-cascade transition.

Here we imply that one cascade can be the saturation transition, the falling transition or the common valley transition. Actually, the saturation transition is also the common valley transformation because here there exists a common valley. Then we shall speak here about the generalized common valley. Then there is the generalized common valley and the falling transition.

Certainly, the multi-common valley can be such a cascade. In this cascade at some may be finite zone several valleys are treated as one common channel. It is also possible that the set of common channels with the given channel can change - at some zone there is one set, at another zone there is another set. But in this common valley under the κ-convexity there will be only one leading pair of the neighbor channels.

As the result we see that in the binary case there is only one leading cascade which is the falling transition or the generalized common valley.

We have examined only the stationary solutions. The relaxation of the distribution n to the stationary solution can be easily studied since in all situations the stationary solution n_{st} is known. Then one can linearize equation on $n - n_{st}$ and get

$$\frac{\partial n}{\partial t} = Ln$$

where L is a differential operator (or in finite differences) on ν_i. Then one can get the relaxation time as the minimal eigenvalue of the linear operator L in the evolution equation by the iteration procedures

$$Trace(L), \ \ Trace(L^2), \ \ Trace(L^3), \ \ etc.$$

of the standard numerical methods.

In reality all operators in the rhs of kinetic equations are reduced to the square approximations. Then the eigenvalues and eigenfunctions are known. Eigenfunctions are the Hermite's polynomials or the Generalized error-functions.

86

Main results

One can see that the problem to get even the stationary rate of nucleation is rather complex. Below we present the sequence of actions to fulfill this task:

1. We determine all channels and find the channel with a minimal activation barrier. Determine its height F_{cm}

2. We determine the rate W_a/W_b. Choose components to have $W_a < W_b$ If $W_b/W_a < exp(1)$ there will be a Stauffer's solution with F_{cm}. If there is an opposite situation one has to continue consideration.

   Suppose that we have the binary case and the κ-convexity. The last property is rather ordinary but it simplifies the consideration. Then the procedure will be the following

   (a) Instead of channels determine the valleys. D We determine also all ridges. We enumerate valleys to have $\xi_i < \xi_j$ for $i < j$. We enumerate ridges to have $\xi_i < \xi_j$ for $i < j$. For every neighbor valleys we determine the source valley i and the destination valley $i + 1$. Below we shall consider the one-cascade transition.

   (b) We determine the possibility of the saturation transition: there is ν_a satisfying conditions:

   $$\nu_a < \nu_{acs}$$

   $$\nu_a < \nu_{acr}$$
   $$F_r(\nu_a) - \Delta_t < F_{cm}$$

   If these conditions are satisfied we determine the point of the saturated transition ν_a^* by equation

   $$F_d(\nu_a^*) = F_r(\nu_a^*) - \Delta_t$$

   This gives
   $$F_* = F_d(\nu_a^*)$$

   (c) We determine the possibility of the common valley transition: there exists ν_a with properties

   $$\nu_a < \nu_{acs}$$

$$\nu_a > \nu_{acd}$$

$$F_s(\nu_a) = F_d(\nu_a) < F_r(\nu_a) - \Delta_t$$

The last condition determines only one point ν_a^{**} of the common valley transition with a maximal intensity. This value will be the saddle point of the unified valley. Here we determine

$$F_{**} = F_s(\nu_a)$$

If the equilibrium valley transition takes place there is no need to consider the falling transition. If it does not exist then we consider the falling transition.

(d) The falling transition takes place when there is ν_a satisfying conditions:

$$\nu_a < \nu_{acs}$$

$$\nu_a > \nu_{acd}$$

$$F_d(\nu_a) < F_s(\nu_a)$$

$$F_r(\nu_a) - F_s(\nu_a) \leq \Delta_t$$

Conditions

$$F_r(\nu_a) - F_s(\nu_a) = \Delta_t \qquad F_d(\nu_a) < F_s(\nu_a)$$

determine the point of transition ν_a^{***} and the free energy

$$F_{***} = F_s(\nu_a^{***})$$

(e) To see what transition is more profitable one has to compare F_{cs}, F_*, F_{**} and F_{***} and to choose the minimal value

$$F_{ch} = min(F_{cs}, F_*, F_{**}F_{***})$$

This will be the free energy corresponding to this valley as the source valley. Then one has to take the minimum over all valleys and to determine the free energy of nucleation F_f. Then the rate of nucleation is rather approximately given by

$$J = \exp(F_f)ZW_a$$

where the Zeldovich' factor Z contains the normalizing factor of the equilibrium distribution.

(f) If there are two approximately equal minimal values of free energies between F_{cs}, F_*, F_{**} and F_{***} then one has to add the quantity $\ln(d(F_r - F_s)/d\nu)$ to the free energy of the falling transition. Certainly, the last quantity shifts the point of transition but approximately one can take it at the old point.

The analysis presented above gave the following new results

- The free energy of the embryo is found including the surface excesses and the clear interpretation of the generalized chemical potential is given. The variables giving the simple form of the free energy is found and their connection with the initial natural variables is shown (section 1). The similarity of the form of the near-critical energy to the situation without surface excesses is shown (section 1). The correction order of the Renninger-Wilemski's effect is shown (section 1).

- The hierarchy in the near-critical region is shown (section 2).

- The impossibility of the essential difference between the Reiss' formula ad the Stauffer's formula in capillary approximation is shown (section 3).

- The possibility to change valleys during the evolution is shown. The discrete analog of Trinkaus' solution is presented and investigated (section 4).

- The possibility to have one united valley instead of several initial ones is shown. It is shown that the height of the effective activation barrier is changed in comparison with the heights of barriers in the initial channels. Thus, the rate of nucleation will be radically changed (section 5)

- The possibility to change the valley and to reach the post-critical zone already from the pre-critical transition is shown (section 6). This form a special type of the equilibrium saturation transition. This transition also leads to a new special value of effective height of activation barrier.

- All possible transition are classified. It is shown that the tree mentioned types cover the variety of possible transitions.

Here only the main new results are outlined. An application of the presented theory to the concrete binary and multicomponent systems will form the subject of a separate publication.

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